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A STUDY OF THE SUPERCOOLED FUSIONS AND SOLUTIONS OF SODIUM THIOSULPHATE.

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THE general phenomena of supercooling and supersaturation, as well as of metastability in general, have been so thoroughly described and discussed in Ostwald's "Lehrbuch der Allgemeinen Chemie"[1] that it is wholly unnecessary to go into any general treatment here. Since the appearance of the last volume of the Lehrbuch, two papers having an important bearing on the subject have appeared.[2] The relationship of the results of previous investigation to our results will be taken up in a later portion of this paper. The investigations described in the following pages were carried out with the hope of throwing light on some of the many conditions that influence the separation of sodium thiosulphate from its metastable solutions and fusions. In the course of the work the fact was developed that sodium thiosulphate was capable of existing in a far greater number of forms than had hitherto been known. In order to assist in the ready comprehension of the main features of the investigation it will be well to first describe these forms, and to give a general idea of the methods by means of which they may be obtained.

[1] Vol. II, Part I, p. 516; Vol. II, Part II, pp. 347, 705, 773.

[2] Jaffé: *Ztschr. phys. Chem.*, **43**, 565; Morse and Pierce: *Proc. Am. Acad.*, **38**, 625.

THE FORMS OF SODIUM THIOSULPHATE.

Ordinary commercial thiosulphate of sodium is a pentahydrate, and is always formed in the process of crystallization at room temperature in open vessels. This substance we will call the α-form. In addition to this there are two other forms of the pentahydrate, which we have called the β- and the γ-form. The β-form has been described by Parmentier and Amat,[1] while the γ-form is hitherto undescribed.

The β-form is most readily obtained by sealing the α-form in a glass tube, heating for a few minutes at from 80° to 100° in a water-bath, and then cooling strongly. The fusion usually solidifies into the β-form with considerable promptness, at temperatures between 10° above and 20° below zero. It exists in the form of long needles and is readily distinguished from the α. It is readily convertible into the α by opening the tube, and dropping in a small crystal of the latter. The transformation then progresses through the tube bodily and offers a very pretty illustration for lecture purposes. Parmentier and Amat obtained the substance from supersaturated solutions instead of from fusions. They give analytical evidence that its composition is that of a pentahydrate

As to the conditions which are most favorable for the formation of the γ-form we are not as yet in a position to say much. This form was discovered quite accidentally, forming occasionally in tubes that did not readily yield β on cooling to low temperatures. There are indications also that the presence of a small excess of water in the tube inclines to the formation of the γ. In appearance the γ is quite different from either the α or β. It forms a very compact and opaque appearing mass, while both the other forms are more or less translucent. It undergoes complete transformation into solution and a lower hydrate at temperatures a few degrees above zero, while the β begins to liquefy at a little above 30° and the α at about 49°. We have no analytical evidence as yet that the γ is really a pentahydrate, but the fact that it is formed by the complete solidification of the fused α shows that it is not a hydrate with less than 5 mols of water to 1 of thiosulphate. It cannot be a cryohydratic mixture, because it is stable at temperatures somewhat above zero. Its conduct on fusion is not such as to lead to the belief that it is a mixture of a hydrate with more than

[1] *Ber. d. chem. Ges.*, **17** (3), 198 ; *Compt. Rend.*, **98**, 735.

5 mols of water, with one with less than five. The evidence then points rather strongly to its being a third modification of the pentahydrate, and until further evidence is obtained we shall consider it as such.

Parmentier and Amat give the melting-points of the α- and β-forms as 32° and 49° respectively. It required but little observation to show us that neither form showed a true melting-point. On the other hand, both go over in the neighborhood of the temperatures mentioned in saturated solutions and lower hydrates. In the case of the α this is very easy to see, as the crystals of the corresponding lower hydrate are of markedly different form from those of the α. In the case of the β the difference in the appearance of the crystals is very slight, but as the salt shows the phenomenon of incipient fusion at near 30°, and as the temperature must be raised some 8° or 9° above this in order for the fusion to become complete, there was little doubt as to the nature of the transition. The solubility data in the following paper give added confirmation of the fact that in neither case is there true fusion, but that both the α- and β-forms go over into lower hydrates and saturated solution on being heated to incipient liquefaction.

The conduct of the γ-form is wholly analogous. When it is warmed to a few degrees above zero, it begins to liquefy, and only after the temperature has been raised to some degrees above the point of incipient fusion does the solution become clear of residual crystals. The appearance of the residual crystals from the γ is quite different from that of either of the other lower hydrates mentioned.

A fourth lower hydrate is obtained when α is fused and allowed to stand at room temperature for a day or two. This lower hydrate forms in very large transparent crystals, often only one in a tube and rarely more than two or three. It is very soluble, as it is formed only in very small quantity.

In addition to the three forms of the pentahydrate there are then four different lower hydrates of sodium thiosulphate. For convenience and brevity we have named these as follows: The one which forms at room temperatures from clear fusions (the last one mentioned above) is called the *a*-form, that formed by partial fusion of the α is called the *b*-form, that formed by the partial fusion of the β is called the *d*-form, and that formed by the

partial fusion of the γ is called the c-form. Data as to the composition of these lower hydrates, in so far as they have been obtained, are given in the following paper.

THE SUPERCOOLING PHENOMENA.

The a or commercial sodium thiosulphate is well known as a substance which shows the phenomenon of supercooling or supersaturation in the liquid state. In the following work we used altogether fusions and not solutions. In such a case as this, however, a fusion may be looked upon as merely a solution whose composition is that of the solid salt. The phenomenon of supercooling is readily observed. The a-form, for example, remains solid on warming until the temperature of 49° is reached. If a portion of the salt be warmed until complete fusion has resulted, for which purpose it is necessary to heat to about 60°, and then allowed to cool, re-solidification does not occur at 49°, nor at any temperature until about +10° has been reached, and in many cases not until —20° or lower has been reached, provided the entrance to the fused mass of particles of the solid a is not permitted, and leaving out of account the formation of a or b for the present. The easiest and surest way of avoiding contamination with a is by sealing the tube before fusion. Thus the substance is kept in a liquid state through a long range of temperatures at which the solid is distinctly the more stable form.

When such a supercooled mass is brought to solidification by lowering the temperature sufficiently it is *never* the a-form which is produced, but usually the β, and sometimes, though comparatively rarely, the γ. In the course of this work we have made observations on some hundreds of tubes, and in no single case has the spontaneous formation of the a been observed. a has been found very rarely in some of the tubes, but in all such cases careful search showed the presence of a crack or of a hole in the tube through which the inoculation could have taken place. As has been stated, in the vast majority of cases the β-form was the one to appear, while occasionally the γ was observed. The temperatures at which solidification occurred were widely distributed, as also the length of time required for the starting of the solidification. Without going into details, the following summary will show what has been observed in a general way as to the supercooling and supersaturation of the fusions and solutions of all of the seven different forms of the salt with which we have worked.

(1) The α-form shows supercooling most markedly, and in no case has it been possible to produce this form in a sealed tube, either from its fusion or from any of the other forms. The metastable limit in respect to this form seems to lie at a very low temperature.

(2) Fusions supercooled as to β (at all temperatures below 30° a fusion of the α is also supercooled as to β) are very readily obtainable, but may almost invariably be forced to the spontaneous formation of the solid β by cooling to sufficiently low temperatures for a sufficiently long time.

(3) Such fusions of α or of β as are very resistant to the formation of β frequently yield γ. The γ, when once produced, shows a very marked tendency to go over spontaneously into β, if kept for any considerable length of time.

(4) All fusions of α or β (or γ) are supersaturated as to the a-form at temperatures below about 32°, and a practically always appears in such tubes when the appearance of β or of γ has not been already forced, provided the tubes have not been heated for too long a time and at too high a temperature (see later).

(5) If α is fused to a liquid free from crystals, that is, if it is heated to temperatures somewhat above 55° until all crystals of the b form have passed into solution, but not much higher, the fusion frequently, and as a matter of fact, commonly yields the b spontaneously on cooling, thus being apparently labile. This may possibly be due to there being left minute indiscernible crystals of the b in the fusion. Actual supercooling as to the b-form does occur, however, in all tubes that have been heated to 60° or higher, and such fusions do not immediately deposit the b-form. Sometimes tubes that have not been heated too high deposit b after a few hours or days. This is without doubt a case of genuine supercooling, as in the case of tubes that have been inoculated with b, the growth is immediate and rapid, the whole apparent deposition being complete in about five minutes.

(6) By reference to the solubility curves in the following paper it will be seen that the system consisting of b and saturated solution is supercooled as to α at temperatures below 49° and as to d at temperatures below 32°, while at temperatures below about 31° it is supercooled as to β. Neither the transformation into α nor into d has been observed, which means that the solution with the

b crystals may be very strongly supercooled as to both of these forms. On strong cooling, the transformation to β is not uncommon.

(7) In marked contrast to the above phenomena is the conduct of the *d*-form. This, in contact with the saturated solution, as produced by the warming of the β to about 35° or so, seems rarely, if ever, to become supercooled as to the β. So soon as the temperature falls below its transition point into β the transition occurs. This was shown very clearly in the attempts to follow the solubility of the *d* at temperatures below 30°.

(8) On the other hand, the transition of the *d* into the *b*, with rising temperature, which, according to the solubility curves, should take place at about 32°, has never been observed. This is manifestly a very clear case of the superheating of a solid, a phenomenon which is very rare.

(9) The conduct of the γ and *c*-forms has as yet been only superficially examined.

The bulk of the work described in the present paper was carried out in order to find, if possible, some regularities in the conditions under which the β forms from supercooled fusions, although incidentally some observations were made on some of the other forms, which give more important results than those made on the β. We have, in the main, limited ourselves to a study of the influence of the variation of the following conditions:

(*a*) The previous formation of β in the same tube.

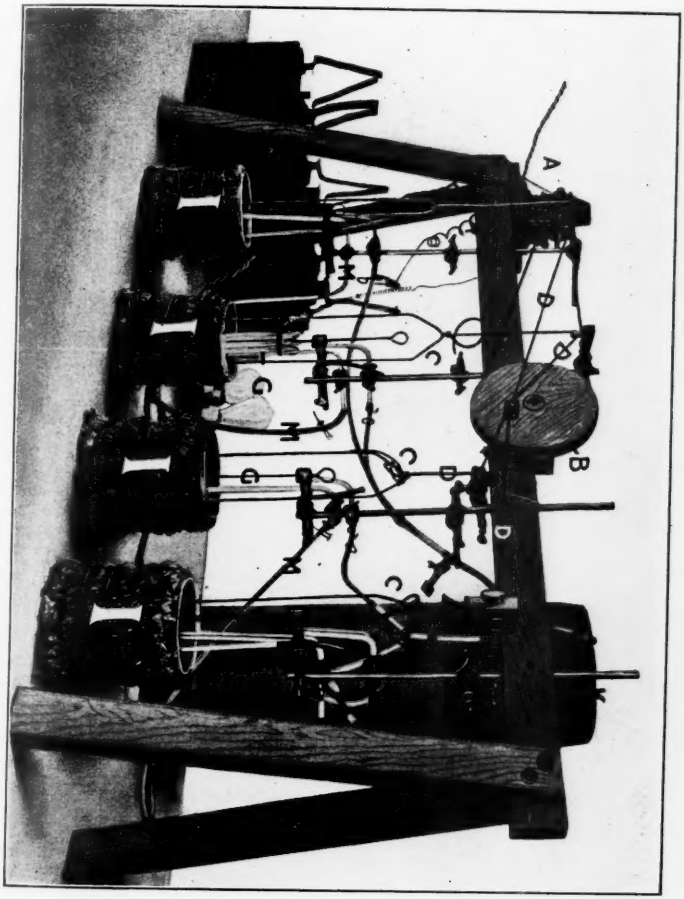
(*b*) The rate at which the tubes were cooled.

(*c*) The temperature to which the tubes had been heated.

(*d*) The length of time which the tubes had been heated.

THE APPARATUS.

All observations were made upon samples of the substances contained in sealed glass tubes of about 6 mm. internal diameter, and 18 to 20 cm. long. As it was necessary to have always at hand a number of baths whose temperatures could be regulated to within something less than a degree, the device shown in the accompanying figure was built. The baths were made of battery jars wrapped with felt. For temperatures above zero the regulation was accomplished by merely adding cold or warm water, as necessary. This, with occasional attention, was sufficient. For the lower temperatures salt solutions of different concentrations in contact with ice were used. With the aid of the automatic


A
B
C
D
E
F
G

stirring arrangement little difficulty was experienced in holding the temperature sufficiently constant for hours. The details of the apparatus may readily be worked out from the figure and its accompanying key.

THE METHOD OF OBSERVATION.

All of the tubes were numbered and a careful record was kept of the treatment that each had received. In the following tables the procedure for each series of tubes is, in general, sufficiently indicated to make any specific description unnecessary. The appearance of a letter α, β, γ, *a*, *b*, etc., in any column indicates that under the conditions specified in the table that particular form appeared. In cases where time data were taken they are indicated at the caption of the table, or in some other way.

The following abbreviations are used in the tables:

A star (*) indicates that the tube was still clear, *i. e.*, free from crystals under the conditions corresponding to the position in the table.

A dash (—) indicates a continuation of the condition specified in the next space above the one where the dash occurs.

A dagger (†) indicates that the tube was broken. This occurred frequently upon the formation of γ, and also with tubes that had been heated for a long time.

TABLE I. SERIES II.

Time of heating, ten minutes. Allowed to stand five minutes at room temperature.[1] Figures give the temperature at which β formed. The cooling was so regulated that the range from +10° to −20° was compassed during an afternoon. A corresponding set of tubes heated to 60°, and not reported here, gave *b* with a single exception, on cooling from the first fusion (of α).

	Tubes heated to 80° C.								
Tube.	9	10	11	12	13	14	15	16	Average.
First fusion, Jan. 22..	−17	−17	−14	−8	−12	−8	−12	−12	−12
Second fusion, Feb. 2	— 9	−15	— 9	−9	−10	−1	— 5	†	— 8
Third fusion, Feb. 4..	— 9	−10	−14	−4	— 8	−6	γ −18	—	— 8
Fourth fusion, Feb. 5	−17	— 8	−16	0	†	−6	†	—	— 9

	Tubes heated to 100°.								
Tube.	17	18	19	20	21	22	23	24	Average.
First fusion, Jan. 22 ..	−14	−19	−19	−14	†	−12	−19	−14	−15
Second fusion, Feb. 2.	−16	†	— 1	−15	—	†	−14	— 1	— 9
Third fusion, Feb. 4 ..	γ −16	—	— 1	−14	—	—	— 5	0	— 5
Fourth fusion, Feb. 5 .	†	—	−18	+ 1	—	—	−15	— 8	−10

[1] This was done in almost all cases, in order to be certain that small crystals of some form were not left which would start immediate crystallization, in which case the tube could not, of course, be considered as supercooled.

TABLE II. SERIES III.

Time of heating, ten minutes. Stood five minutes at room temperature. Tubes held for one hour at each of the temperatures indicated in column 1.

	Heated to 60° C.								Heated to 65° C.								Heated to 70° C.								Heated to 80° C.								Heated to 100° C.							
Tube.	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72
+10°	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	β	*	*	*	*	*	*	*	*	*	*	*	*	*	*	β	*	*	*	β
+ 5°	*	*	*	*	*	*	*	*	*	*	*	*	*	*	β	*	*	*	*	*	—	*	*	*	*	*	*	*	*	*	*	*	*	*	*	—	β	*	*	—
0°	*	*	*	*	*	*	*	*	*	*	*	*	*	*	—	*	*	*	*	*	—	*	*	*	*	*	*	*	*	*	*	*	*	*	*	—	*	—	*	—
— 5°	*	*	*	*	*	*	β	*	*	*	*	*	*	*	—	*	*	*	*	*	—	*	*	*	*	*	*	*	*	*	*	*	*	*	*	—	*	—	*	—
—10°	*	β	β	*	β	β	—	β	*	*	*	*	*	*	—	β	*	*	*	β	—	*	*	*	β	*	β	*	β	*	*	*	*	β	β	—	*	—	*	—
—15°	β	—	—	β	—	—	—	—	*	*	†	*	β	β	—	—	β	β	β	—	—	*	β	β	—	β	—	β	—	β	*	*	β	—	—	—	β	—	β	—
—20°	—	—	—	—	—	—	—	—	β	β	—	γ	—	—	—	—	—	—	—	—	—	β	—	—	—	—	—	—	—	—	β	γ	—	—	—	—	—	—	—	—

TABLE III. SERIES IV.

Time of heating, sixteen hours. Stood five minutes at room temperature. Tubes held for one-half hour at each of the temperatures indicated in the first column. In this series complete observations were carried on at 10°, 5°, 0°, and —5°, but as no tube showed any crystallization at any of these temperatures, the data for these temperatures is put into one row in the table. This is also the case in Table IV.

	Heated to 60° C.								Heated to 70° C.								Heated to 80° C.								Heated to 100° C.							
Tube.	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
+10° to —5°	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
—10°	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	β	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
—15°	γ	*	β	β	β	β	*	*	*	β	β	β	*	*	*	—	*	*	β	*	*	*	*	*	*	*	*	β	β	*	*	β
—20°	—	*	—	—	—	—	*	*	*	—	—	—	γ	γ	β	—	β	*	—	γ	β	*	γ	*	†	†	*	—	—	*	*	—

TABLE IV. SERIES IV.

Time of heating, three and one-half days. Stood at room temperature for five minutes. Tubes held for one-half hour at each of the temperatures indicated in the first column.

	Heated to 60° C.								Heated to 70° C.								Heated to 80° C.								Heated to 100° C.							
Tube.	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76
+10° to −5°	†	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	†	*	*	*	*	*	*	†	†	†	*
−10°	—	*	*	*	*	*	*	*	β	β	*	*	*	*	*	β	*	*	*	*	*	—	*	*	†	*	*	*	—	—	—	†
−15°	—	*	β	—	β	β	β	β	—	—	*	*	β	*	*	—	β	*	β	*	*	—	*	*	—	*	*	*	--	—	—	—
−20°	—	β	—	β	—	—	—	—	—	—	*	β	—	*	β	—	—	β	—	β	β	—	β	*	—	*	β	β	—	--	—	—

TABLE V.

Time of heating, ten minutes. Tubes then allowed to stand at room temperature. Tubes heated under these conditions to 50° and 55°, gave *b* immediately, most of them showing residual crystals of *b* on removal from the bath. They are therefore omitted from the table.

	Heated to 50° C. Series II.				Heated to 65° C. Series III.				Heated to 70° C. Series III.				Heated to 80° C. Series II.				Heated to 100° C. Series II.			
Tube.	39	40	41	42	9	10	11	12	13	14	15	16	43	44	45	46	47	48	49	50
Feb. 12.....	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
		b		*b*																
Feb. 13	*	—	*	—	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Feb. 15.....	*b*	—	*	—	*b*	*b*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Feb. 17.....	—	—	*	—	—	—	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Feb. 18.....	—	—	*	—	—	—	*a*	*a*	*	*a*	*a*	*	*	*	*	*	*	*	*	*
Feb. 19.....	—	—	*	—	—	—	—	—	*	—	—	*a*	*	*	*	*	*	*	*	*
Feb. 20.....	—	—	*	—	—	—	—	—	*a*	—	—	—	*a*	*a*	*a*	*	*	*	*	*
Feb. 22.....	—	—	*	—	—	—	—	—	—	—	—	—	—	—	—	*a*	*	*	*	*
Mch. 21	—	—	*a*	—	—	—	—	—	—	—	—	—	—	—	—	—	*a*	*	*a*	*a*
Apr. 4.....	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	*a*	—	—

TABLE VI. SERIES III.

Time of heating, sixteen hours. Tubes then allowed to stand at room temperatures.

	Heated to 60° C.				Heated to 70° C.				Heated to 80° C.				Heated to 100° C.			
Tube.	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96
Mch. 1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Mch. 14	*	*	*	*	*	*a*	*	*	*	*	*	*	*	*	†	*
Mch. 21	*a*	*	*a*	*	*	—	*	*	†	*	*	*	*	*	—	*
July 4..	—	*	—	*a*	*	—	*	*	—	*	*a*	*	*	*	—	*
July 19.	—	*	—	—	*	—	*	*	—	*	—	*	*	*	—	*

DISCUSSION OF THE RESULTS.

Although the investigation was primarily upon the conditions for the appearance of the β-form, much more decisive results have been obtained from the study of some of the others. But as the bulk of the data refers to the β, it will perhaps be as well to discuss it first.

(*a*) The influence of the previous formation of β in the same tube upon the ease with which it would appear a second time was quite extensively studied. The results obtained were not of sufficient certainty to warrant any very definite conclusions, and the large mass of data obtained is not given. There seemed to be a fairly constant tendency for the appearance of the β to occur the second time at a somewhat higher temperature than at first. Since the first appearance of the β was always from a fusion of the α, and the second from a fusion of the β, it would seem that the previous formation of the β might have had some influence. Table I gives the results of one series of experiments along this line. It will be seen that while the average temperatures of fusions after the first are somewhat lower than those for the first, nevertheless there is considerable variation among the individual results. The observations were made under most unfavorable conditions, and before we had any experience. They will be repeated in order to avoid certain sources of trouble which our experience has shown to exist.

(*b*) The rate at which the tubes were cooled was also quite extensively investigated, the results for the most part being negative in so far as any influence on the temperature of formation of the β is concerned. One thing was noticed, and that was that tubes which had been heated to 60° or 65° only, and which would be expected to yield the *b*-form in from one to three or four days

at room temperature, would yield β instead, if they were rapidly cooled. The formation of β was never observed above 10°, and all fusions which, if cooled, would have given β (or possibly γ) gave a when held at room temperature for a sufficiently long time, unless owing to the low temperature of heating, b appeared, or unless owing to high heating, a was barred from forming (see later). In the latter case nothing appeared. The rate of cooling may, therefore, determine which form shall appear, but so far as we have yet seen it has no marked influence on the temperature at which a form appears.

(*c*) The temperature to which the tubes have been heated also has relatively little influence on the temperature at which the β appears, although, as will be seen later, of very great influence in the cases of some of the other forms. Tables II, III and IV give the results of three series of observations of this sort. In every case it will be seen that it makes but little difference whether the tubes had been heated to 60°, 70°, 80° or 100°; the appearance of the β is scattered over a considerable range of temperature, and is quite irregular. The work of Jaffé[1] has shown conclusively that the length of time that a supersaturated solution is held at a given temperature is of great influence upon its crystallization; that is, in the present case there were doubtless many tubes which did not solidify until 20° below zero was reached, which would have solidified at higher temperatures if they had been held at them for a sufficiently long time. All that we have attempted is to maintain practically constant conditions of cooling.

(*d*) The influence of the length of time that the tubes were heated is also shown in the same tables, II, III and IV. In Table II the tubes were heated for ten minutes, in Table III for sixteen hours and in Table IV for three and one-half days. In Tables III and IV the procedure on cooling was practically the same as in Table II, but as no cases of solidification occurred in these series at temperatures above —10° the results of the cooling from +10° to —5° are condensed into one row in the tables. The results are readily seen. In the case of the ten-minute heating there were a considerable number of scattered solidifications at relatively high temperatures and some of them occurred as high as at 10°. In the cases of longer heating no solidification occurred above —10°. The effect of long heating is thus to considerably

[1] *Loc. cit.*

restrict the range of temperature within which solidification occurs. Table III is noticeable for the large number of appearances of γ. We have no notion why this should have been. There is no noticeable difference in the results in Tables II and III which would indicate either that the influence of heating was complete at the end of sixteen hours or else that the jump from sixteen hours to three and one-half days was not sufficient to cause any further appreciable difference.

To summarize, the results obtained from the study of the solidification of the β are, for the most part, negative, although a very distinct influence is noticed as a result of long heating, in that sporadic solidifications at relatively high temperatures are excluded.

THE CRYSTALLIZATION OF THE *a*- AND *b*-FORMS.

Considerable data on these forms was obtained incidentally to the study of the β. In addition a few series of observations were carried out directly on these forms. In this case the observations are limited to the temperature and time of heating and these forms have shown themselves much more sensitive to these influences than did the β.

Temperature of Heating.—Tables V and VI give the results of two series of experiments to determine the influence of the temperature of heating on appearance of the *a*- and *b*-forms. In Table V the tubes were heated at the temperatures given for ten minutes, and then allowed to stand at room temperature. It will be noticed that two of the tubes heated to 60° formed *b* on the same day, a third three days later, while the fourth formed *a* something more than a month later. This formation of *a* is exceptional, as we have worked with many tubes heated to 60° and they almost invariably give *b* on the first day or within a few days after, provided they have been heated for only a short time. Of the tubes heated to 65° two formed *b* on the fourth day and two did not form *b* at all, but *a* appeared at the end of six days. All of the tubes that were heated to still higher temperatures refused to give *b*, but sooner or later gave *a*. The length of time required for the appearance of *a* increases very rapidly with the temperature. In Table VI, where the period of heating was longer, no *b* was formed in any of the tubes, and the *a* shows an increasing disinclination to form after higher heating.

Time of Heating.—The same tables show the influence of this condition: In Table V the heating was for ten minutes, and in Table VI for sixteen hours. The formation of *b* is prevented altogether by the longer heating. Also the first *a* to form was after two weeks, instead of less than one in the short heating, while even after four months every tube that had been heated to 100° for sixteen hours remained perfectly clear, save one that cracked as a result of the prolonged heating. An inspection of the table will show very clearly that in spite of the fact that a single tube which had been heated to 70° formed *a* earlier than did any that had been heated to 60°, there is, on the whole, a distinctly increasing disinclination to form the *a* with increasing temperature of heating.

This is about all of the facts that we have obtained that permit of being put into coherent form at present. We shall next briefly discuss a working hypothesis that has suggested itself and then attempt to show how it accounts for the above facts, as well as for a considerable number of interesting isolated observations that we have made.

HISTORICAL.

Starting upon considerations based upon the continuous form of the theoretical curve for the transition of liquids into vapors, and the existence of theoretical metastable limits in this particular case, Ostwald has developed a very reasonable theory for cases of supercooling and supersaturation as well (see above citations in the Lehrbuch). Up to the present time, however, no success has attended the many attempts to experimentally determine this metastable limit for any case excepting one, where the supersaturation is produced by means of chemical reaction in gelatine.[1] In fact, it is generally recognized that there are a great many disturbing influences, *i. e.*, influences which cause the given transition to occur before the metastable limit has been reached, and the bulk of the work has resulted in discovering and defining some of these influences. In the case of the condensation of supercooled water vapor an electric charge is known as a potent factor in causing the reaction in a body of vapor. In the case of supercooled liquids and supersaturated solutions, sudden jarring will frequently start the transition, and dust particles have been more or less commonly supposed to have this power. The bulk of the

[1] Morse and Pierce: *Proc. Am. Acad.*, **38**, 625.

research, however, tends to show that dust is inoperative, unless it contains solid particles of the substance that is to crystallize.

Both before and after the suggestion of the metastable limit there are found many hypotheses to explain the spontaneous crystallization of supercooled and supersaturated systems. Thus Lehmann[1] suggests that when a solid is fused there remains a thin layer of the substance next the walls of the vessel, which is of molecular dimensions, and unfused. There is required a considerably higher temperature than that of the melting-point in order to eliminate this. As to the many objections to this hypothesis nothing need be said here (*cf.* Schaum and Schönbeck[2]). DeCoppet[3] suggests a molecular-kinetic explanation of the spontaneous crystallization of supercooled solutions, in that he considers that as the molecules have to unite to form the crystalline aggregate which can start the crystallization, it is largely a matter of uncertainty under just what conditions the crystallization will start, as the molecules must first come into a favorable configuration in order to form the aggregate.

Jaffé worked mainly upon supersaturated solutions of potassium nitrate, and came to the very interesting conclusion that the limit to which the solution can be supercooled is greatly extended by repeated filtration of the solution. Thus the most concentrated solution that could be maintained in the supersaturated state at 20° for any length of time was 51 per cent., unless the solution was first repeatedly filtered. When this was done it was found possible to keep 57 per cent. solutions for about the same length of time. Jaffé explains his results as follows: There are contained in the solution nuclei (Keime) which are capable of starting crystallization sooner or later, and these are of such dimensions that they may be, at least in part, filtered off by passing the solution through cotton wool. As to the source and nature of these nuclei Jaffé says but little.

Schaum and Schönbeck[4] point out the difference in conduct of fusions of benzophenone, when they are made under different conditions. We shall recur to this interesting work later.

THE NUCLEAR HYPOTHESIS.

The hypothesis which we offer in explanation of the results of our own work, and of many of the phenomena observed by others,

[1] Drude's *Annalen*, **2**, 659 (1900).
[2] *Ibid.*, **8**, 652 (1902).
[3] *Ann. chim. phys.* (5), **6**, 275 (1875).
[4] *Loc. cit.*

we shall call the nuclear hypothesis. We start with Jaffé's notion of nuclei, but assign to the existence of these a definite cause, and to their origin, a definite source. We consider them to be residues left upon the breaking-down of the crystalline structure of the solid itself, upon fusion or solution.

Crystals are usually looked upon as aggregates of smaller aggregates, and the smallest fragment of a crystal is still a crystalline aggregate. It seems reasonable to consider, in the light of the work of Ostwald and others, that one of these crystalline aggregates would be capable of starting immediate crystallization in any supercooled fusion or solution of itself. Crystalline aggregates cannot, therefore, be present in any supercooled liquid, which means that a substance once thoroughly fused or dissolved must be free from them.

Although the phenomena of supercooling demand that all crystalline aggregates shall have disappeared when complete fusion or solution has occurred, it does not necessarily follow that they shall all have become transformed into the homogeneous liquid. It is imaginable that, although the breaking-down of the gross crystalline structure is a discontinuous process, taking place at a definite temperature, there are nevertheless left in the liquid either fragments of crystalline aggregates, amorphous particles of the substance, or particles in the colloidal state, or perhaps some other heterogeneous conditions. We assume, in absence of any good reason to the contrary, that the residues are fragments of the crystalline aggregates, and are to be looked upon as solid particles. This assumption is wholly tentative, but has certain advantages from the standpoint of clearness of presentation.

Concerning the dimensions of these nuclei, all that can be said is that from Jaffé's work they seem to be of such a size that they are, at least in part, entangled in cotton wool fibers, although it may be that only such of them as are already entangled in dust particles are capable of being filtered out. Although in themselves incapable of starting crystallization, not being fully possessed of the crystalline structure, they may, under certain conditions, unite to form crystalline aggregates, and thereby cause the crystallization to start.

Owing to the general disintegrating action of heat the above described nuclei would be more or less rapidly destroyed by more or less prolonged heating at higher temperatures. Thus, on the

basis of the nuclear hypothesis, there are two possible methods of removing nuclei, at least in part, namely, filtration and heating. Also the addition of a foreign substance might bring about such destruction. There are many recorded cases of marked increase in the possibility of supercooling upon the addition of small quantities of foreign substances, *e. g.*, alcohol to benzophenone. Some nuclei may naturally be more sensitive to the action of high temperatures than others, whence, in order to bring about the same degree of "sterilization," longer heating, or heating to higher temperatures may be required in some cases than in others.

The possibility of two or more nuclei uniting to form a crystalline aggregate increases with falling temperature, and would be more or less a matter of chance unless the concentration of the nuclei were relatively large. This may account, to some extent, for the irregular results usually obtained. We give at present no theoretical grounds for the assumption that the aggregates are more prone to unite at lower temperatures than at high. The phenomenon might be explained as due to action between a single nucleus and the homogeneous liquid, and not between two or more nuclei.

The possibility of starting crystallization will also depend upon the concentration of the nuclei in the solution. Thus concentrated solutions will be more liable to spontaneous crystallization, not only because they are more supersaturated, but also because of the greater concentration of the nuclei.

If it is assumed that there are definite forces which tend to bring the nuclei together into aggregates, it is clear that this orientation may be assisted by shaking and jarring, just as, for example, iron filings are assisted in taking on figured positions in the magnetic field by the same influences. This offers a possible explanation of the common phenomenon of spontaneous crystallization resulting from these causes, and does not interfere with the notion that these same influences may cause local transgressions of the metastable limit.

One more assumption is necessary to make the nuclear hypothesis cover all the facts which we wish to bring under it, namely, that as different substances give different nuclei just so different polymorphic forms of the same substance and different hydrates of the same substance may give different nuclei, and these different nuclei may be capable of existing alongside of one

another. It by no means follows that the nature of the nuclei in a fusion of a given polymorphic form may be predicted from the nature of the form. For example, the α-thiosulphate does not seem to give any nuclei that are capable of regenerating the same form because, so far as our experience goes, α is never regenerated except as a result of inoculation with a bit of itself. On the other hand, β seems to give chiefly nuclei that regenerate itself.

It may be mentioned that it is possible to explain the phenomena in question on the assumption that all the nuclei from a given substance are the same, and that different concentrations of them and different temperatures are more favorable for the production of the various possible aggregates. The data at hand are not sufficient to enable us to see any advantage in that point of view, and for the present we assume that the nuclei are different, as this assumption has many advantages in clearness and concreteness.

The nuclear hypothesis, as above stated, may seem, in some respects, rather crude, but it is offered simply as a working hypothesis, subject to change or rejection at any time. The hypothesis has thus far been very useful, and it was only by its use that we were able to introduce anything like order into the classification of our experimental results. We shall now give, in some detail, the application of the hypothesis to the explanation of some of the phenomena that we have observed, as well as of some of the observations of Schaum and Jaffé.

(a) From fused α-sodum thiosulphate, so far as our observations go, any one of four forms may separate, according to the conditions of fusion and the subsequent treatment. These forms are the β and γ (pentahydrates), and the a (monohydrate) and b (dihydrate). Never thus far have any of the other forms been observed to form from fused a. In the terms of the nuclear hypothesis we should say that the fused a might contain the nuclei corresponding to these four forms, and either no others or else others in such a small concentration that their influence is never apparent. As to the γ there is as yet no evidence on which to base any assertion. The nuclei of the β-form do not become effective in any case observed until the temperature is dropped to about $+10°$, and they seem to be not much affected by very considerable heating. However, on heating for sixteen hours or more all cases of solidification above $-10°$ seem to be eliminated (Tables

II, III and IV). The nuclei of *b* are, on the other hand, very sensitive to heating. Tubes become practically completely "sterilized" against *b* by heating for ten minutes to 70° and for sixteen hours at 60° (Tables V and VI). The *a* nuclei conduct themselves similarly, although not so sensitive as the *b* sort. Practically complete sterilization occurs after heating for sixteen hours at 100° (Tables V and VI).

(*b*) Fusions of different polymorphic forms and of different hydrates conduct themselves differently. Strictly speaking, what we have called a fusion of *a* is in reality a solution formed from *b*, because the *a* becomes transformed into *b* at some temperature below that at which a clear solution is produced. In the same way a so-called fusion of β is a solution prepared from *d*. Now the two solutions prepared in these different ways conduct themselves in a wholly different manner as regards their supercooling. While that from *a* (or *b*) yields, according to conditions, *a* or *b* at room temperatures and β at low temperatures (sometimes γ) the conduct of the fusion from β conducts itself as follows, the results being based on the conduct of twenty-one tubes of β, heated to 43°; a single tube gave β immediately, undoubtedly on account of incomplete fusion. A second gave, after seven hours, a crystal of a very slow growing substance, from its conduct undoubtedly a lower hydrate, but neither *a*, *b* nor *d*. It is as yet a matter of uncertainty as to what the substance is. It may be a form still different from those described, or possibly it may be the form which we have called *c*, with which we are not as yet sufficiently familiar to recognize it under all conditions. All other tubes remained perfectly clear for over four days. At this time nine of them were taken and cooled at intervals of 5°, and for fifteen minutes at each temperature. Of these nine tubes three gave β at 0°, five gave β at —5° and the other one gave β almost instantly at —15°. The remaining ten tubes were kept, as before, at room temperature, and observed from time to time, with the following results: One week after the time of fusion six of the tubes showed crystals of *a*, while the remaining four are still clear at the time of writing—two weeks after fusion.

Thus fusions of β conduct themselves differently from those of *a* in the following respects:

(1) They never yield *b*.

(2) They may yield a substance (possibly *c*) which has never been observed to form from fusions of *a*.

(3) They show very considerably less inclination to yield *a* than do fusions of *a* heated for the same length of time (compare Table V), even though the latter have been heated to temperatures from 20° to 40° higher.

(4) They form *β* much more readily than do fusions of *a*. This was also shown, although less markedly, in the results given in Table I, the reason probably being that in that series the fusion of the *β* was carried on at much higher temperatures than in the present one.

(*c*) Schaum and Schönbeck found similar conditions to exist in regard to benzophenone. This substance exists in two forms, the stable and the metastable. Either form may result from supercooled fusions, according to conditions. When the metastable form was once obtained it conducted itself very differently in different cases, sometimes going over into the stable form almost immediately after solidification, sometimes going over into the stable form within an hour, and sometimes requiring much longer time. It was apparently the rule, however, that if a sample did not go over into the stable form within an hour it remained permanently in the metastable form. The authors, therefore, divide the different samples of the metastable benzophenone which they obtained into three classes: (1) Those going over within fifteen minutes are called *unstable;* (2) those going over in less than an hour, but requiring more than fifteen minutes, are called *stable;* (3) those requiring more than an hour, and which do not, in general, go over at all, are called *very stable.* In the following table is given a brief summary of the results. Under T is the temperature of heating; under θ is the time of heating; under N is the total number of tubes that were under observation in each series; under A the percentage of the tubes that remained liquid after cooling to room temperature, *i. e.*, that showed supercooling at all; under B the percentage of the supercooled tubes that solidified into the stable modification on cooling in ether-carbon dioxide mixture; under C, D and E are the percentages of the supercooled tubes that, under the same treatment, solidified respectively into the unstable, stable and very stable modifications of the metastable form.

θ. Minutes.	T. °C.	N.	A. Per cent.	B. Per ct.	C. Per cent.	D. Per ct.	E. Per ct.
15	50–52	260	17	88.6	11.4	0	0
180	50–52	139	54	89.3	10.7	0	0
15	100	112	99	64.9	22.5	7.2	5.4

These phenomena allow of a satisfactory and fairly simple explanation in terms of the nuclear hypothesis. The temperature of heating in the first two series is only 2° to 4° above the melting-point of the ordinary benzophenone, and, therefore, no considerable sterilization occurs even with relatively long heating. Thus after three hours' heating at this temperature only about one-half of the tubes remain in the supercooled state at room temperature, while with only fifteen minutes' heating less than one-fifth remain supercooled. On the other hand, heating for fifteen minutes at 100° sterilizes practically all of the tubes against solidification at room temperatures. The similarity in conduct here with that observed as to the appearance of the *b*-form of sodium thiosulphate in tubes heated to various temperatures and for various times is very striking. We obtained many results with the *b*-form which are not included in the tables. The substance of these results was that heating even for a considerable length of time at temperatures only 2° to 5° above the temperature of clear fusion yielded tubes which almost invariably gave *b* at room temperatures, and usually in a comparatively short time.

Schaum's results further show that of those tubes which persisted in the supercooled state at room temperatures, the large portion crystallized in the stable form on cooling to —79°, *i. e.*, in ether-carbon dioxide solution, but that while about 90 per cent. of the 50° to 52° fusions showed this conduct it was shown by only about 65 per cent. of the 100° fusions. This requires no further explanation than that given for the solidification at room temperatures.

Those supercooled tubes which did not solidify into the stable modification gave the metastable form, and this was shown by about 10 per cent. of the 50° to 52° tubes and 35 per cent. of the 100° tubes. Thus the fused ordinary benzophenone is a liquid containing two sorts of nuclei, one capable of causing solidification under certain circumstances of the stable form, and the other sort capable of bringing about solidification in the metastable form. In just fused benzophenone the stable nuclei so preponder-

ate in influence that the bulk of the samples solidify immediately into the stable form, but on heating for a longer time or at a higher temperature, increasing numbers of samples are restrained from solidifying at room temperature. The metastable nuclei, *i. e.*, those capable of combining to form the aggregates necessary for the solidification in the metastable form, seem to become efficient only at lower temperatures, and the relative numbers of the two sorts of nuclei, or rather perhaps the relative activity of efficiency of them, will determine into which of the two forms the sample will solidify. Thus the 50° to 52° tubes, in which the stable nuclei still largely preponderate, give the metastable form only in 10 per cent. of the cases, while the 100° tubes give this form in 35 per cent. of the cases. On the basis of the nuclear hypothesis one would readily be able to predict that had the heating to 100° been carried on for a much longer time, or had even higher temperatures been resorted to, complete or nearly complete sterilization against the stable form might have been attained.

Also the appearance of metastable solidifications of differing degrees of persistence is readily explained. If in a tube containing both stable and metastable nuclei a group of the metastable nuclei come into conditions favorable for starting the solidification, and do start it, it is also more than likely that a group of the stable nuclei will also have reached a similar condition and there may be started a stable solidification even before the metastable one is complete. If there happens to be a group in favorable condition, *i. e.*, just ready to start the stable solidification, even after the metastable solidification was complete, it might persist and subsequently start the transformation of the metastable form into the stable. If there were no group of stable nuclei in approximately favorable conditions, the chances for this transformation setting in would be very small after the tube had solidified into the metastable form. Thus metastable tubes of different degrees of stability are easily imaginable. We have observed all of the above phenomena in the case of the β- and γ-forms of sodium thiosulphate. The γ forms relatively rarely, and when it does form is very likely to be assimilated by a growth of β, which may start either before or after the complete solidification into the γ-form.

(*d*) Jaffé found that the effect of repeatedly allowing his supersaturated solutions to crystallize out and then heating to redis-

solve was to considerably increase the degree of supercooling possible. In the light of what has been said it seems probable that this phenomenon is due solely to the heating to which the solution was subjected, and not to the fact of repeated solution and crystallization. At any rate, this is a point which future investigation can readily decide. It is to be said, however, that Schaum noticed the same thing as a result of repeated fusion and solidification, a fact which does not fit into our theory so readily. The distinction between the two cases is as follows: If 50 grams of potassium nitrate are dissolved by warming with 50 grams of water, the solution will contain all of the nuclei corresponding to the 50 grams of potassium nitrate. On crystallization, only a part of the salt will leave the solution, and on re-solution only a small number of nuclei will be re-introduced, and these, as well as those remaining in the solution will be influenced by the heating to bring about re-solution, and a gradually increasing degree of sterilization will result, up to a certain limit. In the case of a liquid that completely solidifies, this is no longer the case. One would expect the same number of nuclei as a result of each fusion, provided the fusion occurred each time under the same circumstances. Even here an explanation is not impossible, but rather forced. The phenomena discussed in the next paragraph, however, do furnish a fairly reasonable explanation.

(*c*) It has been repeatedly observed that when a supercooled liquid crystallizes the crystallization frequently starts from not more than two or three points, and very commonly from only one. These points are frequently on the wall of the tube and in many cases fixed so that crystallization always starts from the same point. Such points are called critical spots and the belief is common that they are due to some peculiarity of the glass itself. We have repeatedly observed, however, that these spots are not necessarily either fixed or located on the wall of the tube. For example, we found one tube in which β had formed, which, if carefully fused at not over 45°, invariably solidified at 5°, and always from a single point. By turning this tube, while the β was in the fused state, and allowing the fluid to flow from end to end of the tube and then cooling, the critical spot would have usually moved to another portion of the tube, sometimes at the wall and sometimes in the midst of the liquid. Schaum found these critical spots of very common occurrence, and also found

that they could be, to a great extent, eliminated by heating. In a general way, and looked at from the point of view of the nuclear hypothesis, any point at which solidification starts would be a critical point. Thus when a sufficiently great number of nuclei come into favorable positions a critical point will be spontaneously formed. Furthermore, it is possible that, since the nuclei are solid particles (may be filtered out), they might easily become entangled occasionally with dust particles, and that an enclosed dust particle might, when the solid was melted, entangle a sufficient number of nuclei to create a spot from which solidification could most readily take place. Such a critical spot once attached to the wall of the tube would be inclined to stay there. The nuclei contained in such a place would also be susceptible to sterilization. Any dust particles that were adhering to the walls before the fusion would also be inclined to stay there, so that there is ample explanation of the fact that the critical points occur very frequently at the walls of the tube. Such critical spots might become gradually disentangled by repeated fusion, and this may explain Schaum's results with benzophenone, mentioned in the last paragraph.

Jaffé noticed a great tendency for solidification to start from points near the bottom of his tubes. We have also noticed this. In about 70 per cent. of the tubes examined, in which β had crystallized, the starting-point was well below the middle of the liquid column. Possibly this percentage would have been larger, if all tubes had been allowed to stand longer in an upright position before forcing solidification. Jaffé very reasonably explains this as due to the settling out of the nuclei.

(*f*) Tammann[1] has investigated the phenomenon of supercooling from a somewhat different standpoint. He determined the number of points at which crystallization started at different temperatures and found a maximum at pretty definite temperatures, which lie within that temperature interval in which the velocity of crystallization increases. Any discussion at this time of the relationship of his work to ours would be premature, and will be left until our data are more complete. We do not, at present, see anything in his results that conflicts with our conclusions.

There are many interesting questions that come up in regard to the possibility of producing supersaturated solutions as a result

[1] *Ztschr. phys. Chem.*, **22**, 306.

of chemical action, and the real function of the gelatine in the production of supersaturation in the case of the Liesegang rings,[1] but the data is too insufficient to permit of intelligent discussion at this time.

The Ostwald Rule and the Metastable Limit.—Ostwald has suggested that it seems to be a fairly general rule that when a supercooled or supersaturated system is forced into transition it is not the stable but the metastable form which separates out.[2] He also gives theoretical grounds for the rule. Wald,[3] in a paper discussing this rule, concludes that it is not thoroughly well founded and predicts that it will be found that the necessary conditions will be discovered, by whose regulation the different forms may be obtained at will. Our results show that at least a start has been made in that direction.

Although we do not intend to enter on any considerable discussion of this point here, a few words may not be out of place. The existence of a metastable limit, in the first place, presupposes in the case of supercooled liquids, a perfectly homogeneous phase. In other words, any crystallization or solidification that is due to nuclei of any sort, cannot be said to be due to a transgression of the metastable limit in the strict sense of the word. Ostwald himself[4] points out that when once the metastable limit is transgressed the whole body of the liquid *en masse* would be affected at once, although he likewise points out that it is easy to imagine that the metastable limit might be reached locally, as a result of local disturbances—as of pressure. But the main point at present is that in the case of the nuclei we are dealing with a disturbing factor, and no true metastable limit can be reached until their influence is eliminated. It seems probable that under ordinary circumstances it may become possible to control the particular form in which a substance may solidify, and the Ostwald rule need not necessarily apply. In case the conditions for the reaching of the true metastable limit were attainable the rule might possibly hold, although Wald does not think so. The above considerations do not apply to the possible case that a perfectly homogeneous liquid spontaneously forms nuclei; but the nuclei which we assume to produce spontaneous crystallization are apparently not produced in this way.

[1] See Morse and Pierce: *Loc. cit.*
[2] *Ztschr. phys. Chem.*, **22**, 306.
[3] *Ibid.*, **24**, 503.
[4] See Lehrbuch.

SUMMARY.

The more important results of this investigation may be summarized as follows:

(1) Seven different forms of sodium thiosulphate are described, of which three are pentahydrates and four hydrates with less than 5 molecules of water of crystallization. The general conditions for the production of the various forms are given.

(2) Considerable progress has been made in determining under what conditions some of these forms may be obtained from supercooled solutions and fusions.

(3) In determining these conditions the whole previous history of the sample is of importance, mainly in three respects: (*a*) The form of the salt from which the solution or fusion is prepared; (*b*) the time of heating; (*c*) the temperature of heating.

(4) A fairly satisfactory hypothesis has been devised to account for the phenomena observed, as well as for many observations of Jaffé and particularly of Schaum. The hypothesis also suggests many lines of investigation. It is the intention to carry out a systematic study of these phenomena in this laboratory in order to determine to what extent the hypothesis is useful.

NOTE.—Some days after the above was written I received the copy of the *Zeitschrift für physikalische Chemie*[1] containing Füchtbauer's paper on the "Spontaneous Solidification of Supercooled Liquids." From a rather hasty reading I find nothing in the experimental part which seems necessarily to conflict with the conclusions of the above paper, while the theoretical treatment seems not to cover many of the phenomena that were observed with sodium thiosulphate.—*S. W. Young.*

STANFORD UNIVERSITY, CAL.,
July 19, 1904.

ON THE COMPOSITION AND SOLUBILITY OF THE HYDRATES OF SODIUM THIOSULPHATE.

BY S. W. YOUNG AND W. E. BURKE.

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AS HAS been shown in the previous paper, sodium thiosulphate is capable of existing in a variety of different forms, some of them being polymorphic pentahydrates and others hydrates with

[1] **48**, 549.

less than 5 mols of water of crystallization. It was the purpose of the experiments to be described in this paper to determine the composition of these different forms, as well as their solubility at different temperatures. The solubility determinations above all are of prime importance to the complete understanding of the phenomena of supercooling discussed in the previous paper, because from a knowledge of these data it is possible to determine at what temperatures a given form is stable or metastable with regard to another, since the metastable form must always have the greater solubility. The temperature at which the solubilities of two forms become the same is the transition point for those two forms, at which they become equally stable, and may exist indefinitely long in contact with one another.

Although the work has not been entirely completed, that which has been done has such direct bearing on the results of the work described in the previous paper that it seems well worth while to publish it at this time.

(1) DETERMINATIONS OF COMPOSITION.

The determination of the composition of any of the metastable forms of sodium thiosulphate offers very considerable difficulties. Under ordinary conditions all other forms are metastable in respect to the *a*, that is, the commercial salt, and upon the slightest inoculation with this, any one of them is readily and rapidly converted into the *a*. How, then, to remove any one of the metastable forms from the solution out of which it had crystallized, and to dry it so that any reliable determinations of its composition could be made was a very considerable problem. A number of methods were tried, including centrifuging under such conditions that the salt was protected as well as possible from inoculation. But the results were of no value; being irregular and not approximating to any rational formula. In all cases there was ample evidence that the samples had become converted to the *a*, undoubtedly mixed in some cases with some lower hydrate or with the anhydride.

Finally the attempt was made to dry the salts at temperatures above the melting-point of the *a*, *i. e.*, at above 49°. The temperature chosen for the drying was 55°, at which temperature it was naturally impossible for any *a* to form. Of course, this did not preclude the possibility of some other transformation

taking place. No difficulty was experienced from such sources with the *b*, but with the *a* only approximate results could be obtained, as will be shown.

Composition of β.—No determination of the composition of this was made. Its formation by complete solidification of the fused *a* and its conduct as a chemical individual are sufficient to show it to be a pentahydrate. And furthermore, Parmentier and Amat,[1] who obtained the substance from solutions, analyzed it and concluded that such was the case.

Composition of γ.—There is every reason to believe that the γ-form is also a pentahydrate,[2] although no analysis has as yet been obtained. Being stable only at temperatures in the neighborhood of 0° and below, special devices must be resorted to in working with it. We hope to get direct evidence as to its composition in the future.

Composition of a.—Samples of *a* were obtained by filling a large test-tube two-thirds full of molten *a* and then drawing off the top and sealing it. The whole was then immersed in water near the boiling-point for about fifteen minutes. After several days the large crystals of *a* appeared and after further standing acquired their maximum size. They were accumulated near the bottom of the tube, and adhered rather firmly to the wall so that, on inverting, the crystals remained above the mother-liquor, and could thus be thoroughly drained. The tube was then opened in the inverted position, the tip being kept under water, by which the heavier mother-liquor was replaced by pure water. A bath at 55° was held in readiness and the tube removed from the water, held sufficiently long for most of the water to run out, then brought to the upright position and immersed to the neck in the 55°-bath. This accomplished, all danger of inoculation by *a* is past. A glass tube connected with the suction was introduced into the tube to facilitate drying, which was carried on until the crystals began to show signs of efflorescence at the edges. Samples were then removed, weighed, and titrated with standard iodine solution. From these data was calculated the number of molecules of water to one of thiosulphate. The values found were: I, 1.213; II, 1.132; III, 1.191; IV, 1.110—corresponding fairly closely to the formula $Na_2S_2O_3.H_2O$. It seems likely that

[1] *Ber. d. chem. Ges.*, **17** (3), 198.

[2] See previous paper, p. 1390.

partial transformation to *b* may have occurred during the treatment, and it is doubtful if better results can be obtained without great expenditure of time.

Composition of b.—The composition of *b* was determined the same way as that of *a*, except that it was not necessary to seal the tube, a good rubber stopper being in this case sufficient. This was because of the relatively short time that it was necessary to wait for the deposition of the crystals, which, with the *b*, was sufficiently complete in half an hour. In order to obtain the *b* crystals the fusion of the *a* was never carried above 55°, as it had been shown in the previous work that such fusions were most favorable for the production of *b*. Otherwise the drying and analysis were carried out as above. Two determinations gave the number of molecules of water to one of thiosulphate as follows: I, 2.003; II, 2.006. The substance is thus a dihydrate, having the formula $Na_2S_2O_3.2H_2O$.

Composition of c.—No determinations have as yet been made.

Composition of d.—Only a single determination of the composition of *d* is at hand, and that was made in a rather crude manner. When it was first noticed that there was such a substance formed by the partial fusion of *β*, a portion was hastily taken, thrown on clean filter-paper, rapidly pressed out, a sample taken and titrated. The result obtained was 4.18 molecules water to 1 of thiosulphate, which would seem to indicate that the substance was a tetrahydrate. If the *d* is a tetrahydrate, then the trihydrate formula would be the only one left for the *c*, unless this should contain a fractional number of molecules of water, or be dimorphic with some of the other forms. Our information is too incomplete to enable us to draw any definite conclusions, as yet, and these uncertain compounds will be further investigated.

(2) DETERMINATIONS OF SOLUBILITY.

The determinations of the solubility of the sodium thiosulphate in its various forms were made in the usual manner, by placing suitable amounts of water and commercial thiosulphate in tubes of about one-half inch internal diameter, sealing in the flame, giving such treatment as to produce the desired form, and then rotating in the thermostat at the desired temperature until saturation was attained, sampling and analyzing. Preliminary determinations showed that saturation was very quickly reached, *i. e.*,

after about fifteen minutes or so. In the actual determinations, however, no measurements were made on tubes that had not been rotated for at least an hour. Preliminary determinations were also made with both supersaturated and undersaturated solutions, but as both gave identical results in a very short time it was not in general the practice to make determinations in both ways.

When everything was ready for the determination the tube was removed from the rotating device and placed in a holder fastened in the thermostat tank, so that the top of the tube projected somewhat above the water. A cut was then made and the top broken off. The samples were taken in a small weighed pipette, weighed and titrated with standard iodine. In order to avoid taking up small crystals with the solution, a piece of small rubber tubing, about one inch long, was attached to the tip of the pipette and a wad of cotton wool packed fairly tightly into it. This served as a filter.

Solubility of the α.—This was naturally the easiest of all the forms to work with, being the most stable. All that was necessary was the filling and rotating of the tubes, the sampling and analysis. The results are given in Table I. In the last column are given the

TABLE I.—SOLUBILITY OF α-SODIUM THIOSULPHATE.
(Commercial pentahydrate.)

Temperature.	Parts $Na_2S_2O_3$ in 100 solution.	Average.	Parts $Na_2S_2O_3$ in 100 H_2O.	Mulder's results.
10°	37.38			
10°	37.37	37.38	59.69	....
10°	37.38			
20°	41.20			
20°	41.17	41.20	70.07	69.00
20°	41.23			
25°	43.17			
25°	43.06	43.15	75.90	75.00
25°	43.21			
30°	45.19			
30°	45.24	45.19	82.45	82.00
30°	45.13			
35°	47.70			
35°	47.71	47.71	91.24	89.00
35°	47.71			
40°	50.84			
40°	50.79	50.83	103.37	98.00
40°	50.85			
45°	55.32			
45°	55.35	55.33	123.87	109.00

results of Mulder,[1] which show fair agreement with ours, except at higher temperatures. As the original of Mulder's paper is not accessible to us, we do not know just what his method may have been, but probably it was the usual method of those times in which flasks containing the substances were shaken occasionally at the desired temperatures, and then portions poured off through filters held at, nearly as possible, the same temperature.[2] If this were the case, it would readily account for his low results, particularly at high temperatures.

Solubility of β.—In order to obtain tubes containing β and solution we always started with α and water. These were sealed up in the tubes, and heated to 100° and then cooled to force the crystallization of β. In doing this two difficulties were encountered. In the first place the tubes all showed a marked tendency toward the formation of γ instead of β. This seems characteristic of tubes containing an excess of water. In the majority of cases the γ-tubes went over into β on long standing, although some were very persistent in the γ-form. The second difficulty arose from the very great temperature coëfficients of the solubility, and from the fact that the β crystallized out in very fine needles. This made it very difficult to judge of the amount of water which should be added in order that a given tube might be worked with at a given temperature. A very small quantity of the β-crystals is sufficient to make a stiff broth of the whole solution, so small an amount, in fact, that by raising the temperature 2° the solubility will have increased to an extent sufficient to carry the broth over into a clear solution. Of course, samples can be taken only from tubes that, at a given temperature, lie between these two conditions, so that the difficulty of obtaining a tube that can be used at a given temperature becomes considerable.

A further difficulty is met with in taking the sample (and this is true of all other forms than the α) in that the solution, being supersaturated in respect to α, is likely to become inoculated with that salt and thus render the tube worthless. The difficulty was, to a great extent, avoided by keeping the pipettes in an air-bath at 60° for some time before using, and working with great rapidity after a tube was opened. Transformation to α after the pipette is once filled is, of course, of no importance. Results with β are given in Table II.

[1] *Scheik. Verh.*, 1864. p. 84.
[2] See Kremers: Pogg. *Ann.*, **94**, 271.

TABLE II.—SOLUBILITY OF β-SODIUM THIOSULPHATE.
(Pentahydrate.)

Temperature.	Parts $Na_2S_2O_3$ in 100 solution.	Average.	Parts $Na_2S_2O_3$ in 100 H_2O.
20°	49.34		
20°	49.39	49.38	97.55
20°	49.40		
25°	52.11		
25°	52.26	52.15	108.98
25°	52.09		
28°	54.49		
28°	54.48	54.48	119.69
29.5°	55.85	55.85	126.50
30°	56.58		
30°	56.68		
30°	56.62	56.57	130.26
30°	56.57		
30°	56.53		
30°	56.53		

Solubility of a.—The tubes for this purpose were prepared by sealing up the commercial salt without water, heating for a few minutes in boiling water and allowing to stand a few days until the *a* appeared. With such tubes, determinations could be made up to 30° only, since at that temperature the saturated solution of the *a* has the composition of a pentahydrate. The results obtainable were, however, sufficient for present purposes. The data are given in Table III.

TABLE III.—SOLUBILITY OF *a*-SODIUM THIOSULPHATE.
(Monohydrate.)

Temperature.	Parts $Na_2S_2O_3$ in 100 solution.	Average.	Parts $Na_2S_2O_3$ in 100 H_2O.
20°	62.03		
20°	62.20	62.11	163.92
20°	62.10		
25°	62.76		
25°	62.71	62.73	168.32
30°	63.54		
30°	63.53	63.53	174.20

Solubility of b.—The tubes for these determinations were obtained by fusing the *a* in tubes, without water, and allowing the temperature to rise no higher than 55°. In this way the *a* was entirely destroyed and the residual crystals of *b* caused rapid crystallization as the tubes cooled. The results are given in Table IV.

TABLE IV.—SOLUBILITY OF *b*-SODIUM THIOSULPHATE.

(Dihydrate.)

Temperature.	Parts $Na_2S_2O_3$ in 100 solution.	Average.	Parts $Na_2S_2O_3$ in 100 H_2O.
20°	55.15		
20°	55.16	55.15	122.68
25°	55.97		
25°	56.05	56.03	127.43
25°	56.06		
30°	57.17		
30°	57.11	57.13	133.27
30°	57.11		
35°	58.18		
35°	58.11	58.13	138.84
35°	58.10		
40°	59.16		
40°	59.19	59.17	144.92
50°	62.23		
50°	62.32	62.28	165.11
50°	62.30		

Solubility of d.—The solubility curve of this substance was obtained by simply carrying tubes containing β to temperatures above its transition point into saturated solution and *d*. The results are given in Table V. It was found impossible to carry out any determinations below the transition point, as supercooling of *d* in respect to β does not seem to occur.

TABLE V.—SOLUBILITY OF *d*-SODIUM THIOSULPHATE.

(Probably tetrahydrate.)

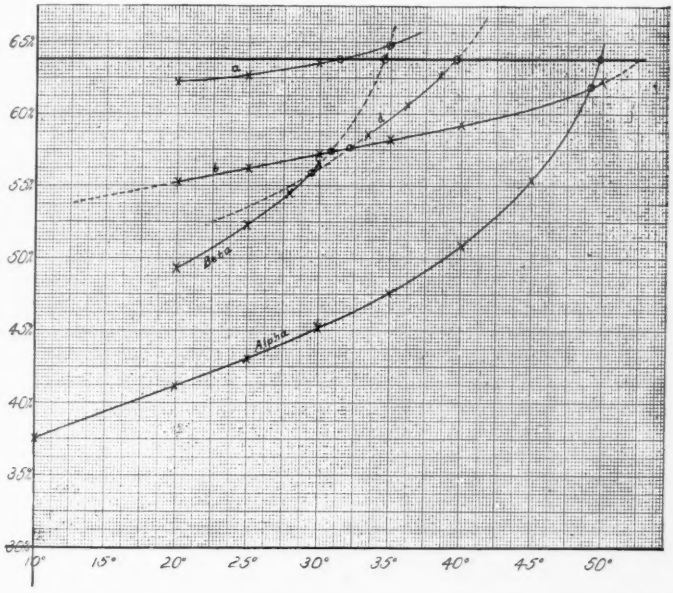
Temperature.	Parts $Na_2S_2O_3$ in 100 solution.	Average.	Parts $Na_2S_2O_3$ in 100 H_2O.
33.5°	58.55		
33.5°	58.64	58 59	141.48
36.2°	60.51		
36.2°	60.54	60.51	153.23
36.2°	60.49		
38.6°	62.84		
38.6°	62.71	62.80	168.82
38.6°	62.85		

Solubility of γ and c.—No data have been obtained as yet.

(3) THE SOLUBILITY CURVES.

In the accompanying set of curves the solubility data, above given, are plotted. The $\times$ marks actual determinations, or rather

the average of these, while transition points and points of complete solution in pentahydrate fusions are marked with circles. The dotted lines are extrapolated. The horizontal line just below 64 per cent. is the line of composition of pentahydrate. As all of our determinations were made with samples containing at least as much water as the pentahydrate, this line forms the limit of all of these determinations. Determinations at still higher concen-



trations of the lower hydrates are under way. The point at which the solubility curve for any pentahydrate cuts this line will evidently be the true melting-point of the pentahydrate. The curves show that the true melting-point of neither the α nor the β can be reached without passing transition points, *i. e.*, without passing through a superheated state. Neither of these melting-points seems to be practically attainable. The two transition points into lower hydrates are readily seen from the diagram.

An interesting relationship is noticed in connection with the curves for the *b* and the *d*. A transition point is shown at about

31.7° between these two hydrates in contact with saturated solution in such a way that *d* is stable at lower and *b* at higher temperatures. The range for the stable existence of the *d* is thus limited to the range of temperature lying between 30° and 31.7°, but *d* was observed and its solubility measured at temperatures as high as 38.6°. Thus between 31.7° and 38.6° the *d* exists in a superheated state. As is well known, this is a very rare phenomenon. It is possible that, since the three transition points at 30°, 30.5° and 31.7° lie so close together, we have been deceived as to their exact location, but this seems hardly probable.

The chief value of the curves at present is that they define very exactly the fields of supersaturation and supercooling for the forms already studied. To interpret the curves briefly, we see that at temperatures below 31.5° (on *a* curve) a fused pentahydrate is supersaturated or supercooled in respect to all forms considered in this paper. Above 31.5° supersaturation in regard to *a* ceases. At 34.5° supercooling in regard to β ceases, while above 39.5,° 49.5° and 53° supercooling or supersaturation as to *d*, *a* and *b*, respectively, ceases. The detailed interpretation need not be given here, as any one interested can make it for himself.

We shall extend the investigation to all the remaining forms, including the anhydride.

STANFORD UNIVERSITY, CAL.,
July, 1904.

A STUDY OF REVERSIBLE OXIDATION AND REDUCTION REACTIONS IN SOLUTIONS.

BY EUGENE P. SCHOCH.

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INFLUENCE OF THE CONCENTRATIONS OF THE COMPONENTS UPON THE EQUILIBRIUM IN ACIDIFIED SOLUTIONS OF IODINE, POTASSIUM FERROCYANIDE, POTASSIUM FERRICYANIDE AND POTASSIUM IODIDE.

THE investigation here described was undertaken for the purpose of studying a reversible oxidation reaction in solution. The reaction used was selected on the basis of the following considerations:

(1) The action should be simple.

(2) Each component should be present in relatively large amount, so that its concentration could be varied to a large extent.

(3) The approach to equilibrium from either side should take place with a measurable velocity.

I selected, for investigation, the reversible reaction between iodine and potassium ferrocyanide in acidified solution because (1) the action is probably simple, since it appears to be a mere transfer of ionic charges as per the equation

$$2Fe(CN)_6'''' + I_2 \rightleftarrows 2Fe(CN)_6''' + 2I';$$

(2) each component may have its concentration varied between wide limits; (3) the action starting with either iodine and ferrocyanide or iodide and ferricyanide, requires one and a half to two hours to obtain equilibrium.

In addition to fulfilling these conditions, this reaction presented the following advantages: (1) The potentials of ferrocyanide-ferricyanide solutions[1] and of iodine-potassium iodide solutions[2] had been measured; and (2) the state in which iodine exists in the potassium iodide solutions had been clearly explained and determined by Jakowkin.[3]

Equilibrium in a reversible reaction is considered to be the result of two opposite actions having equal velocities, and the observed velocity of change of a mixture which reacts reversibly is proportional to the difference of the velocities of the two opposing reactions. The effect of the concentration of any constituent, according to this view, is evidently the same whether the mixture is in or out of equilibrium,[4] and since equilibrium conditions are usually more accurately determinable, it was decided to obtain these before making any velocity determinations. I present below the results obtained in the study of the equilibrium conditions, trusting to be able to follow this soon with another paper presenting the velocity determinations.

Chemicals, Preparation of Solutions, Etc.—The potassium iodide employed was obtained from Kahlbaum, and was found to be free from iodate. A normal solution was prepared practically every day on which it was used.

Potassium ferrocyanide and potassium ferricyanide were both Kahlbaum's "for quantitative work." Half-normal solutions of

[1] Fredenhagen: *Ztschr. anorg. Chem.*, **29**, 396.
[2] Crotogino: *Ibid.*, **24**, 225.
[3] Jakowkin: *Ztschr. phys. Chem.*, **20**, 20.
[4] Van't Hoff's "Vorlesungen Theor. Phys. Chem.," **1**, 182.

these were prepared by weighing out the required amount of salt. The strength of these solutions was also checked by titration with a decinormal solution of iodine, according to Rupp and Schiedt's[1] method, which method I had tested carefully. Both solutions decomposed very slowly,[2] hence fresh solutions were prepared frequently.

For the iodine solution, Kahlbaum's resublimed iodine was employed. Potassium iodide in amount to make exactly a decinormal solution, and iodine for approximately the same concentration, were weighed out and dissolved. The exact titer of the iodine was then found and checked frequently during the progress of the work.

More dilute solutions were prepared from the above as occasion demanded.

Some Preliminary Determinations by Means of Electromotive Force Measurements.—Of the substances put into the reaction mixture—namely, potassium ferrocyanide, potassium ferricyanide, potassium iodide, iodine and hydrochloric acid—only the following are involved in the action: Ferrocyanidions, iodine, ferricyanidions and iodions; and the others (potassions and hydrochloric acid) are *quasi* foreign ingredients. While the main problem is the determination of the influence of the concentration of the main ingredients, it is evidently also necessary to know the influence of the concentrations of these other substances. To determine their influence, electromotive force measurements were made, because the potentials of ferrocyanide-ferricyanide solutions and of iodine-potassium iodide solutions are easily and accurately determinable. The method used was the well-known Poggendorff compensation method. A large accumulator was used as the working element, and its current was passed through two equal resistance boxes of 500 ohms each. An Ostwald capillary electrometer was used for a zero instrument; it was sensitive to 0.0001 volt and less. For comparison, two normal cadmium cells were employed. They had been prepared at different times, and since they agreed to within 0.0001 volt, and the measurements in this paper are only comparative, comparisons with a standard cell were not made. Two normal calomel electrodes were prepared which agreed exactly with each other, and hence were con-

[1] Rupp and Schiedt: *Ber. d. chem. Ges.*, **35**, 2430.
[2] Mathuschek: *Chem. Ztg.*, **25**, 601.

sidered to be correct. They were frequently exchanged in making the measurements, thus guarding against temporary defects in either one. The calomel electrodes, as well as the other electrode vessels and platinized electrodes, were prepared according to directions in Ostwald-Luther's "Hand- und Hilfsbuch."

Influence upon the Potential of Iodine-potassium Iodide Solutions.—As shown by Crotogino,[1] the potential of the iodine-potassium iodide electrode depends upon the fraction of the total iodine which is not combined with the potassium iodide. The per cent. of dissociation in any case may be calculated with the aid of Jakowkin's formula.[2] There appears to be no reason why acidifying the solution should have any influence upon the potential; at most, there might be a slight influence, since the thermic dissociation of hydriodic acid is slightly less than the thermic dissociation of potassium triiodide. Crotogino found this latter to be the case. I also found only a very small difference. A solution, N/4 in potassium iodide and N/100 in iodine, gave 0.001 volt less after acidifying with hydrochloric acid (N/20) than before.

The influence of potassions upon iodine-potassium iodide solutions need evidently not be considered, since the quantity of potassions introduced by the ferrocyanide and the ferricyanide is very small in comparison with that introduced by the potassium iodide.

Influence of Potential of Ferrocyanide-ferricyanide Solutions.—(1) Influence of concentrations of potassions; *à priori,* it is to be expected that large variation in the concentrations of the potassions will cause, at least, some variation in the ionization of the ferrocyanide and ferricyanide, and hence change the potential. Such is the case, but the variation is small. The addition of potassium chloride to ferrocyanide-ferricyanide mixtures in amounts varying from N/2 to N/8 in the resulting solutions produced less than 0.005 volt difference.

(2) *Influence of Acidification.*—The potentials of the neutral ferrocyanide-ferricyanide solutions were first investigated by Schaum, and afterward by Fredenhagen,[3] both of whom applied the results and formula obtained by Peters,[4]

$$\pi = A + \frac{RT}{nF} ln \frac{C\,(\text{ferricyanide})}{C\,(\text{ferrocyanide})}.$$

[1] Crotogino: *Ztschr. anorg. Chem.*, **24**, 225.
[2] Jakowkin: *Ztschr. phys. Chem.*, **20**, 20.
[3] Fredenhagen: *Ztschr. anorg. Chem.*, **29**, 396.
[4] Peters: *Ztschr. phys. Chem.*, **26**, 193.

In this formula A is the value of π when the two substances are present in the same concentration, since the log. of unity is zero. R, T, n and F have the usual significance. The formula enables the calculation of the potential of neutral solutions, the results agreeing to millivolts with the observed values. The formula is evidently based upon the idea that 1 ferrocyanidion changes to 1 ferricyanidion, since the first power of the concentration of both is employed. Hence all mixtures which contain ferrocyanide and ferricyanide in the same ratio should have the same electromotive force, irrespective of the volume of the solution.

Fredenhagen has shown that the potentials of solutions of ferrocyanide-ferricyanide do not change when *slightly* acidified. Nothing is stated anywhere about the effects of stronger acidification. I found that the potential of ferrocyanide-ferricyanide electrodes measured against a normal calomel electrode increases very largely upon acidification, as may be seen from the following trial:

A solution containing 0.01538/N ferrocyanide, 0.00962/N ferricyanide, and 0.50/N potassium chloride, when *neutral*, gave electromotive force = 0.1795 volt; when acidified (= N/20 hydrochloric acid), gave electromotive force = 0.2667 volt.

Though the concentration of the potassions has but little influence upon the potential, yet it was thought best to add them in the form of potassium chloride to correspond to potassions introduced by the potassium iodide in the equilibrium experiments given later on.

Since both $H_4Fe(CN)_6$ and $H_3Fe(CN)_6$ are strong acids, about equally dissociated, it was somewhat difficult to understand why acidification should cause this great difference in potential. Hence it was determined to investigate this further by varying the concentrations should not affect the potential as long as the ratio to our present knowledge of these substances, variations in concentrations should not affect the potential as long as the ratio of the molecules or ions remains the same; in other words, the potential depends only upon the *ratio* of the quantities of ferrocyanide and ferricyanide. Such has been found to be the case in neutral solutions. In acidified solutions (= N/20 hydrochloric acid) the concentration was found to effect the potential extensively, and it appeared that the effect is entirely due to the ferro-

cyanide. When the concentration of the ferrocyanide is kept constant and the concentration of the ferricyanide is varied, the potentials observed agree fairly well with those calculated from the formula,

$$\pi = A + 0.0575 \log. \frac{C\ (\text{ferricyanide})}{C\ (\text{ferrocyanide})}.$$ [1]

TABLE I.—POTENTIALS OF SOLUTIONS CONTAINING 0.50 N POTASSIUM CHLORIDE, 0.05 N HYDROCHLORIC ACID, 0.005 N FERROCYANIDE, AND FERRICYANIDE AS IN COLUMN 1.

Ferricyanide.	Electromotive force observed.	Electromotive force calculated.
0.0025 N	0.259	0.254
0.0050 N	0.2709	Value of A in formula
0.0125 N	0.294	0.2938
0.0250 N	0.3108	0.311
0.0375 N	0.321	0.321
0.0500 N	0.3276	0.328

TABLE II.—POTENTIALS OF SOLUTIONS CONTAINING 0.50 N POTASSIUM CHLORIDE, 0.05 N HYDROCHLORIC ACID, 0.0125 N FERROCYANIDE, AND FERRICYANIDE AS IN COLUMN 1.

Ferricyanide.	Electromotive force observed.	Electromotive force calculated.
0.004 N	0.233	0.233
0.00625 N	0.2436	0.244
0.0125 N	0.2625	Value of A in formula
0.0250 N	0.279	0.2798
0.0375 N	0.2868	0.288
0.050 N	0.294	0.296

With a still larger quantity of ferrocyanide than was used in the second series above, say, 5 cc. N/2 ferrocyanide solution per 100 cc. total solution, the electromotive force obtained with different concentrations of ferricyanide diverge somewhat from those calculated. When, on the other hand, the ferricyanide is kept constant and the concentration of the ferrocyanide is varied, there is no agreement between the observed results and those calculated with the formula.

TABLE III.—POTENTIALS OF SOLUTIONS CONTAINING 0.50 N POTASSIUM CHLORIDE, 0.05 N HYDROCHLORIC ACID, 0.0125 N FERRICYANIDE, AND FERROCYANIDE AS IN COLUMN 1.

Ferrocyanide.	Electromotive force observed.	Electromotive force calculated.
0.004 N	0.2979	0.2904
0.00625 N	0.285	0.279
0.0125 N	0.2625	Value of A in formula
0.025 N	0.224	0.244
0.0375 N	0.1974	0.2355
0.050 N	0.1806	0.227

[1] This formula is derived from the one mentioned before by substituting numerical values for R, T, F, and n and changing to Brigg's logarithms.

The disagreement between the observed results and those calculated with the formula is shown most strikingly by the following series of electromotive force measurements in which the ratio of ferrocyanide to ferricyanide is kept constant, but the concentration of both together is varied. Theoretically the same electromotive force should be obtained in all cases.

TABLE IV.—POTENTIALS OF SOLUTIONS CONTAINING 0.50 N POTASSIUM CHLORIDE, 0.05 N HYDROCHLORIC ACID, FERRICYANIDE AND FERROCYANIDE IN EQUIVALENT AMOUNTS AS GIVEN IN COLUMN I.

Concentration of ferrocyanide and of ferricyanide.	Electromotive force observed.
0.005 N	0.2709
0.0084 N	0.2667
0.0125 N	0.2625
0.025 N	0.2415
0.050 N	0.2205

The indications are that the effect of the ferrocyanide varies as some power of its concentration other than the first—probably the second power. The above figures, however, agree only very roughly with any such calculations, and since the results obtained further on show better agreement, no definite conclusions are based on the above.

Equilibrium Determinations.—To investigate the influence on equilibrium of the members of the reversible reaction under consideration, the concentrations necessary for one equilibrium mixture were first accurately determined. Then, in turn, two of the four substances were kept constant, a third changed to one-half, double, or treble the amount in the first equilibrium mixture and the quantity of the fourth, which is necessary for equilibrium, was then found by trial.

The mixtures were analyzed by determining the amount of iodine present. In general, it is not possible to do this by titration, because more iodine is generated as soon as some iodine is removed. In very dilute solutions, however, iodine and ferrocyanide react *completely*, irrespective of any iodide and ferricyanide present. Hence for every mixture of the four substances there must be an intermediate dilution at which iodine is practically not produced, or a small quantity not absorbed. Theoretically, this is the dilution in which one drop or less of iodine

is in equilibrium with the ferrocyanide, ferricyanide and iodide present. Such dilutions were found experimentally by taking different ratios of ferrocyanide to ferricyanide and different concentrations of potassium iodide in such dilutions that the mixtures would not generate or absorb more iodine in an hour than corresponds to one drop of decinormal solution. Any solution approximating these concentrations will fulfil the above conditions. The following table, V, gives the results thus obtained, and these figures were used in this work:

TABLE V.—SOLUTIONS OF FERROCYANIDE, FERRICYANIDE, POTASSIUM IODIDE, AND HYDROCHLORIC ACID, WHICH PRACTICALLY DO NOT GENERATE OR ABSORB IODINE.

Total volume in cc.	No. cc. N/1 KI solution.	No. cc. N/2 ferrocyanide solution.	No. cc. N/2 ferricyanide solution.	No. cc. N/1 HCl.
375	25	2.5	2.5	5.0
435	25	2.0	3.0	5.0
235	25	3.0	2.0	5.0
160	25	3.5	1.5	5.0
535	25	1.5	3.5	5.0
560	50	2.5	2.5	5.0
326	16.6	2.5	2.5	5.0
175	12.5	2.5	2.5	5.0
340	25	2.5	2.5	10.0
122	25	2.5	2.5	2.0

That thiosulphate in such solutions can be titrated back accurately with iodine was tested carefully. Amounts of thiosulphate, varying from 10 to 25 cc. decinormal solution, were put into each one of the mixtures given in the table above, and titrated back with decinormal iodine solution. It was also ascertained that small quantities of iodine are not taken up by reaction in these solutions. Thus 5 to 15 cc. centinormal solution of iodine were added to each of the mixtures, and when titrated back after a lapse of 5 to 7 minutes, only a negligible loss was observed.

The actual procedure in any titration was as follows: By reference to the table the amount of water necessary for diluting 100 cc. of the solution to be examined was estimated. This amount was put into a beaker, N/10 thiosulphate solution in amount exceeding about 10 cc., the amount necessary for the iodine, was added, the measured amount of sample added quickly with constant stirring and the excess of thiosulphate solution determined with starch and decinormal iodine solution. In all cases the resulting mixture was tested to see if it had been properly diluted.

TABLE VI.—RESULTS OF EQUILIBRIUM EXPERIMENTS WITH ACIDIFIED (= N/20 HCl) SOLUTIONS OF POTASSIUM IODIDE, FERROCYANIDE, FERRICYANIDE, AND IODINE.

	Concentrations (in terms of N/normal solution.)						Values (4) of						
Expt. No.	Ferrocyanide.	Ferricyanide.	Potassium iodide.	Iodine.	Per cent. dissociated iodine. (1)	Total free iodine in terms of 0.0001 N.	$\frac{I_2\ (free)}{(K_3Fe(CN)_6)^2}$.	$\frac{I_2\ (free)}{(KI)^2}$.	$\frac{[K_4Fe(CN)_6]^2}{K_3Fe(CN_6)}$.	$[K_4Fe(CN)_6]^4.I_2$ (free).	$K_3Fe(CN)_6.KI$.	$\frac{[K_4Fe(CN)_6]^2}{KI}$.	Values of $10^9 \times K$ from $K = \frac{[K_3Fe(CN)_6]^4.I_2\ (free)}{[K_4Fe(CN)_6]^2.(KI)^2}$. (3)
1	0.01	0.0072	0.26	0.00973	0.54	0.525	1.0135	0.00078	0.0140	5254×10^{-16}	0.001872	0.000385	150
2	0.01	0.01	0.26	0.01946	0.55	1.070	1.0703	.....	.....	.....	.....	.....	158
3	0.01	0.0123	0.26	0.02919	0.565	1.649	1.0900	.....	.....	.....	.....	.....	161
4	0.01	0.0072	0.125	0.001123	1.145	0.013	.....	0.00082	.....	.....	.....	.....	159
5	0.01	0.0072	0.3744	0.0292	0.393	1.148	.....	0.00082	.....	.....	.....	.....	159
6	0.03	0.0615	0.26	0.00973	0.54	0.525	.....	.....	0.0146	.....	.....	.....	166
7	0.0076	0.0072	0.26	0.02919	0.565	1.649	.....	.....	.....	4945×10^{-16}	.....	.....	157
8	0.01	0.0144	0.13	0.00487	1.17	0.565	.....	.....	.....	.....	0.001872 (2)	.....	162
9	0.0148	0.0072	0.52	0.01946	0.27	0.525	.....	.....	.....	.....	.....	0.000421	179
10	0.00709	0.0072	0.13	0.00487	1.17	0.565	.....	.....	.....	.....	.....	0.000387 (2)	164

Since with the proper dilution all the iodine is taken up by the thiosulphate, and at no moment the iodine in the dilute solution was present in sufficient amount to react appreciably with the ferrocyanide, it is certain that the quantity of iodine in the equilibrium mixture is thus accurately determined.

The equilibrium experiments were carried out by measuring into calibrated 100 cc. flasks the required amount of these substances, filling up to the mark, mixing thoroughly and leaving the flasks in a thermostat from two and one-half to three hours. The thermostat maintained a temperature of 25° C., with variations not exceeding 0.05°. The flasks were almost entirely filled with the solution, and were closed with ground glass stoppers.

In all cases a series of trials with separately prepared mixtures was made until the proportion was found with which the amount of iodine put in remained unchanged. When this had been found, at least one more trial was made with the proportions on the side of equilibrium beyond that from which it was approached. Each final equilibrium determination was duplicated. The results are given in the accompanying table, VI.

NOTES TO TABLE VI.

(1) The concentration of effective iodine, *i. e.*, the portion not combined with the iodine, is found with the aid of Jakowkin's formula

$$\frac{(a-l-x)x}{v(l-x)} = k \ ;$$

where v = volume in liters of 1 gram-molecule of iodine;

a = number of KI gram-molecules in v volume; and

x = fraction of total iodine which is not combined with KI to form KI_3. The mean value for k is 0.00138. However, this value is not absolutely constant, and must be properly changed according to the concentration.

(2) The concentration of free iodine in this experiment is not quite the same as in Expt. 1. This must be borne in mind in comparing results.

(3) At first sight the values of this K do not appear to be as nearly constant as might be desired, but we must not neglect to consider several factors which probably account for this variation:

(*a*) Ferrocyanide and ferricyanide solutions are decomposed by sunlight and other influences.[1] A very small change in the

[1] Mathuschek: *Chem. Ztg.*, **25**, 601.

concentration of either, and particularly in the concentration of the ferrocyanide causes a large difference in the numerical result. Thus, if in Expt. 9 the stock solution of ferrocyanide used had decomposed so as to be 4 per cent. weaker, the value for K would have been 0.00000015.

(*b*) An error is introduced by calculating the thermic dissociation of iodine upon the assumption that only KI_3 is present, whereas the dissociation is undoubtedly influenced by the presence of the acid, so that the quantity of dissociated iodine is probably slightly less, corresponding to the presence of some HI_3. Both of these causes probably operate to produce the extreme value in Expt. 9. I believe, in view of this, the agreement among the values of K is fairly satisfactory.

(4) The selection of the powers of the concentrations to be employed for the products and quotients in columns 8 to 13 was easily done by inspection. The products and quotients give the equilibrium formula,

$$\frac{C^4\,(\text{ferrocyanide})\;C\,(\text{free iodine})}{C^2\,(\text{ferricyanide})\;C^2\,(\text{potassium iodide})} = K.$$

From the equation for the reaction

$$2Fe(CN)_6'''' + I_2 = 2Fe(CN)_6''' + 2I'.$$

The *second* power of the concentration of the ferrocyanide should appear in the equilibrium formula. But since all independent variations possible (see Expts. 6, 7, 9 and 10) require the second power of the concentration of the ferrocyanide in place of the first (hence the fourth power in place of the second), there can be no doubt of the correctness of the formula arrived at. It should also be recalled that electromotive force measurements point to the same result.

SUMMARY.

(1) In this paper has been presented the influence upon equilibrium of the concentrations of potassium ferrocyanide, potassium ferricyanide, potassium iodide, and iodine in dilute acid solutions (N/20 hydrochloric acid). The formula expressing the conditions of equilibrium in such solutions at constant temperatures is

$$\frac{C^4\,(\text{ferrocyanide})\;C\,(\text{free iodine})}{C^2\,(\text{ferricyanide})\;C^2\,(\text{iodide})} = K.$$

(2) Both electromotive force measurements and chemical equilibrium determinations show that the effect of ferrocyanide in acidified solutions is proportional to the square of its concentration where theoretically it *should be proportional to the first power.*

Work on this problem will be continued.

In the experimental work of this paper I have been assisted by Mr. R. C. Pantermühl of this laboratory. I gladly take this occasion to express my appreciation of his assistance.

EQUILIBRIUM IN THE SYSTEM BeO : SO_3 : H_2O.

By Charles Lathrop Parsons.

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The sulphates of beryllium were first studied by Berzelius in 1815,[1] although Vauquelin, in 1798,[2] had already produced a gummy basic sulphate. It was Berzelius who first found the necessary conditions to produce the neutral tetrahydrate, which he considered to be of an acid nature. He also produced basic substances to which he gave the formulas $3BeO.SO_3$, $2BeO.SO_3$ and $6BeO.SO_3 + 3H_2O$. Awdejew,[3] in 1842, first proved the neutral character of $BeSO_4.4H_2O$, carefully purified it and studied its properties in connection with his atomic weight determinations. Weeren,[4] in 1854, again used this salt for the same purpose and claimed that it loses one-third of its water of crystallization as low as 35°. Debray,[5] in the following year, used the properties of the basic sulphates as a means of separation from aluminum and states that the precipitated basic sulphate, on continued washing, left nothing but the hydroxide.

In 1869, Klatzo[6] took up the study of the sulphates and claimed to prepare the salt $BeSO_4.7H_2O$. Atterberg, 1873-74, in his extended study of the compounds of beryllium,[7] again prepared $BeSO_4.4H_2O$ and $BeSO_4.2H_2O$, and assigned the following formulas to the basic compounds prepared by him. $BeSO_4.Be(OH)_2$

[1] Schweigger : *J. Chem. Phys.*, **15**, 296.

[2] *Allgem. Jour. der Chem. Scheerer*, **1**, 590.

[3] Pogg. *Ann.*, **56**, 101.

[4] *Ibid.*, **92**, 91.

[5] *Ann. chim. phys.* (3), **44**, 1.

[6] Inaugural dissertation. Dorpat, *Ztschr. Chem.*, **12**, 129.

[7] *Kongl. Svenska Vet. Akad. Hand.*, **12**, 1 ; also *Bull. Soc. Chim.* (2), **19**, 497, and (2), **21**, 157.

$+ 2H_2O$, $BeSO_4.2Be(OH)_2 + 2H_2O$, $BeSO_4.5Be(OH)_2 + 2H_2O$ and $BeSO_4.7Be(OH)_2 + H_2O$. Topsöe,[1] and Topsöe and Christiansen,[2] in 1873, studied the crystalline form, specific gravity, molecular volume and optical characters of $BeSO_4.4H_2O$. Thomson[3] determined its heat of solution. Nilson and Petterson[4] determined its molecular heat and specific gravity, and also that of the product obtained by drying at 250°, which they considered the anhydrous sulphate. Nilson and Petterson,[5] and Krüss and Moraht[6] again prepared and studied the hydrated sulphates and used the tetrahydrate in atomic weight determinations. The author[7] was unable to obtain satisfactory results from it for the atomic weight of beryllium, mainly owing to a slight but continuous loss of water over desiccating agents.

The following sulphates of beryllium have, therefore, more or less standing in chemical literature:

$BeSO_4$.	$BeSO_4.Be(OH)_2.H_2O$.
$BeSO_4.2H_2O$.	$BeSO_4.2Be(OH)_2.2H_2O$.
$BeSO_4.4H_2O$.	$BeSO_4.5Be(OH)_2.3H_2O$.
$BeSO_4.7H_2O$.	$BeSO_4.5Be(OH)_2.2H_2O$.
	$BeSO_4.7Be(OH)_2.2H_2O$.

Attempts were made to prepare and study all of these substances and any other compounds containing the three components, BeO, SO_3 and H_2O, that might be formed under varying equilibrium conditions.

BERYLLIUM SULPHATE TETRAHYDRATE, $BeSO_4.4H_2O$.

Beryllium sulphate tetrahydrate is easily prepared when the components SO_3 and H_2O are in excess and should always be so made in practice. A very slight excess in solution of the BeO component will prevent the formation of the compound and only a non-crystallizable syrupy mass will result. In the presence of excess of sulphuric acid or the exact equivalent, it crystallizes readily. It is best prepared by dissolving beryllium carbonate or hydroxide in excess of moderately dilute sulphuric acid and evaporating to the crystallizing point. These crystals can then be

[1] *Centrbl.*, 1873, p. 76.
[2] *Ann. chim. phys.* (5), **1**, 5.
[3] *Ber. d. chem. Ges.*, **6**, 712.
[4] *Ibid.*, **13**, 1459.
[5] *Ibid.*, **13**, 1451.
[6] *Ann. chim. phys.*, **262**, 32.
[7] This Journal, **26**, 72.

purified by washing with strong alcohol, re-solution in water, evaporation to a syrup and turning, while hot, into excess of strong alcohol. The solution is at first colloidal, but after some hours the $BeSO_4.4H_2O$ crystallizes out almost completely. By repetition, the last traces of sulphuric acid may be removed; or, more quickly, beryllium oxide may be dissolved in concentrated sulphuric acid in a platinum dish and the excess of sulphuric acid be driven off by a Bunsen burner, held in the hand. Care must be used to heat but little higher than necessary to remove the excess of acid. The mixture of anhydrous sulphate with a little oxide, resulting from its own decomposition, is then treated with water and allowed to stand. While quite insoluble at first, the sulphate will have dissolved in the course of one or two days. Filtration from the undissolved oxide and crystallization yields a product of a fair degree of purity.

Beryllium sulphate tetrahydrate is stable in air having an aqueous vapor pressure equal to or greater than the pressure of its own water of crystallization. Tensimeter experiments show this pressure over phosphorus pentoxide at 20° to be equivalent to 20 mm. of olive oil and to increase rapidly with the temperature. At ordinary laboratory temperatures the pulverized salt slowly but surely lost water in a desiccator over phosphorus pentoxide. Many sets of weighings might be given, showing this slow but continuous loss, but as they bring forth no other fact they are scarcely worth entering in detail. The other properties of the tetrahydrated sulphate have been carefully determined by the authorities cited and need no repetition here.

BERYLLIUM SULPHATE DIHYDRATE, $BeSO_4.2H_2O$.

Beryllium sulphate dihydrate is easily prepared by heating the tetrahydrate to 100°. At this temperature it is fairly stable, but if kept in dry air from 100° to 110° it very slowly loses water. This loss is so slow that it would not be detected in ordinary work, but with sufficient time and careful weighing may be shown to be continuous. In dry air, at ordinary temperatures, it is quite stable. It has, in general, the same appearance and properties as the tetrahydrate.

ANHYDROUS BERYLLIUM SULPHATE, $BeSO_4$.

Two apparent methods present themselves for the preparation of this compound: First, by driving off the water of crystalliza-

tion of the dihydrate, and second, by treating beryllium oxide with concentrated sulphuric acid. The first method was employed by Nilson and Petterson, who claimed it was rendered anhydrous at 250°. Such is, however, far from being the case, for water is given off at temperatures many degrees above this temperature. Repeated experiments, undertaken by me, have shown that there is no sharply defined line between the points where all water is driven off and where sulphuric anhydride begins to be evolved. In fact, they come off together through a considerable range of temperature. A product which is almost anhydrous and which has lost no sulphuric anhydride can be obtained near to the boiling-point of sulphuric acid. The second method, used by Lebeau,[1] is subject to the same objections, but to a less degree, if a very strong acid is used. It is next to impossible to evaporate the last traces of free acid and water resulting from its decomposition without decomposing a small amount of the sulphate, and I have never been able to make a sulphate in this manner which did not leave behind a small amount of insoluble residue after the main portion had been dissolved. The anhydrous sulphate is almost insoluble in water and is stable in dry air. It is gradually acted upon by cold water and more quickly by hot, and apparently has to be converted into the very soluble tetrahydrate before solution will take place. It certainly loses sulphuric anhydride as low as 400° and probably much below this temperature. The last traces are driven off only at a white heat.

BERYLLIUM SULPHATE HEPTAHYDRATE, $BeSO_4.7H_2O$.

Klatzo, in the course of his extended investigation on beryllium compounds, claimed to have produced the sulphate $BeSO_4.7H_2O$ and gives analyses of his product. From acid solution he first separated the normal sulphate $BeSO_4.4H_2O$ and then from a like mixture of substances by making more strongly acid and treating by long evaporation between 18° and 25° over sulphuric acid; first monoclinic crystals of a basic salt were thrown out and following them crystals of the normal $BeSO_4.7H_2O$, a truly astonishing sequence, especially when it is considered that by the evaporation the liquid phase was continually growing more concentrated in sulphuric acid and the higher hydrate was claimed to separate from this more strongly acid solution. Marignac[2] has already

[1] *Compt. Rend.*, **123**, 818.
[2] *Ann. chim. phys.* (4), **30**, 45.

severely criticized certain parts of this investigation and certainly no other chemist has ever made the heptahydrate. A repetition of Klatzo's experiment, which was perhaps unnecessary, yielded nothing but the tetrahydrate. It can be safely stated that there is no evidence of the existence of $BeSO_4.7H_2O$.

Variously modified conditions have failed to yield any other definite sulphates of beryllium than those already mentioned.

BASIC COMPOUNDS.

The normal salts of beryllium are, in general, strongly acid to litmus when in solution and act like acids toward many substances, being acted upon by zinc and some other metals with evolution of hydrogen. They all dissolve large quantities of beryllium hydroxide and carbonate, evolving the carbon dioxide in the latter instance. The quantities of hydroxide or carbonate dissolved are proportional to the concentration in very strong solution, although this is not so apparent when the solutions are dilute. The extent of possible saturation varies with the acid used, but is usually as much as three equivalents of beryllium to one of the acid radical, and in the case of the acetate is nearly six. The addition of water to some of these basic solutions throws down immediately precipitates of a more highly basic character, non-crystallizable and of a gummy nature. On drying at 100° these precipitates are glassy and show no evidence of definite structure under the microscope. The remaining solution itself is also basic in character and its basicity depends on the dilution until a point is reached where the further addition of water throws out no further precipitate. On evaporation, the residues obtained are also gummy non-crystallizable masses and are physically undistinguishable from the basic precipitates except by the fact that they are soluble in water. The precipitates, on washing, continually grow more basic and rapidly approach the hydroxide in composition, although I have never been able to entirely eliminate the acid. To the precipitates themselves and to the residues left in solution, various formulas have been given. As they themselves are never definite in composition it is not strange that different chemists have seldom agreed as to the formulas assigned.

A lack of appreciation of the strong hydrolyzing action of water on beryllium compounds has caused many investigations to fail and has added many beryllium compounds to the literature which

have no existence in fact. Still the normal salts themselves are but slightly dissociated, as Leys[1] and Bruner[2] have shown. In fact, they are not nearly so much dissociated as the corresponding salts of aluminum and iron, which possess the same power in a very much less degree of dissolving their hydroxides and precipitation by water.

This property of beryllium has led to much confusion in its literature, and in the opinion of the author, based upon an examination of many of these so-called basic compounds and upon the results which follow, it is very doubtful if any definite basic compounds of beryllium have been made in which beryllium is the only metal present, with the exception of the basic acetate of Urbain and Lacombe,[3] and others of the same group, as prepared by Lacombe.[4] These latter are a truly wonderful series of compounds, basic in nature, yet made in anhydrous acid. They, too, are hydrolyzed by water and then lose their crystalline character and definiteness of composition. Most of the so-called basic compounds are probably solid solutions of the hydroxide with the normal salt. Precipitated by water the hydroxide occludes large quantities of the normal salt; much of which can be removed by washing, but which, in turn, dissolves and carries some of the hydroxide with it as it is washed out. It is hoped to study more of the precipitates by phase-rule considerations and to arrive at some conclusion regarding the nature of the basic solutions through a study of the migration of the ions and the effect upon the freezing-point.

BASIC BERYLLIUM SULPHATES.

Of the basic sulphates already enumerated as claimed by Berzelius and Atterberg, those of a dibasic and tribasic nature are considered as soluble sulphates, it being possible to dissolve them while the hexabasic and octabasic sulphates are precipitated from the soluble basic sulphates by dilution with water.

SOLUBLE BASIC SULPHATES.

When neutral beryllium sulphate is treated with the basic carbonate, carbon dioxide is evolved and an amount of the base is dissolved, depending on the concentration of the solution. If the

[1] *Ztschr. phys. Chem.*, **30**, 218.
[2] *Ibid.*, **32**, 133.
[3] *Compt. Rend.*, **133**, 874.
[4] *Ibid.*, **134**, 772.

solution of the basic sulphate is fairly concentrated (about 1:3), the final saturation ratio of base to acid is as 3:1. If the solution is quite dilute (1:1000) this saturation ratio does not usually exceed 1.5:1. Solutions have, however, been obtained by washing the insoluble basic sulphates having as high a ratio as 2.1:1, which were apparently not altered by dilution, while others of a less basicity have thrown out small amounts of the insoluble compounds. The conditions causing this variation have not been determined. A very small amount of carbonate dissolved in the normal sulphate takes from it its power of crystallization on evaporation. Accordingly, a substance of any degree of basicity up to tribasic can be produced by evaporation of the corresponding solution and drying the residue. Several of these substances have been produced and analyzed. They separate as gummy glucose-like masses, which, on drying at 100°, are still soft, but on cooling become glassy, hard and brittle, and can be easily pulverized. On heating over a Bunsen burner they swell up to an immense volume, losing water and yielding a glistening foamy mass, which, if ignited over the blast-lamp, is reduced to oxide. The powder itself can be dissolved in a minimum of water depending on its basicity and the solution, if precipitable by water, may be diluted to an amount inversely proportional to its basicity before the more highly basic sulphates, soon to be considered, are thrown out. The less basic are similar in composition, physical and chemical properties with the sulphates left in solution when the more basic of these substances are, by the hydrolytic action of water on dilution, separated into a soluble and an insoluble constituent. The tribasic sulphate is simply the limit of saturation, the dibasic the half-saturated solution at full concentration. There is no other reason at present to consider them as definite compounds, for the ratio base to acid in fully precipitated solutions is seldom, if ever, exactly 2:1, as supposed by Berzelius and Atterberg. On drying at 100° the amount of water left is generally in excess of the theoretical amount necessary to produce the hydroxide, but this has little significance, as the gummy character of the substances makes their complete drying improbable.

The following analyses of these soluble basic powders will serve as examples. Many others were made. Nos. 1 and 2 are of the saturated concentrated solution: Nos. 3 and 4 of the soluble resi-

dues after apparently complete precipitation. Their difference is quite probably due to variation of temperature, as no thermostat was used in this preliminary work.

No.	BeO. Per cent.	SO_3. Per cent.	H_2O. Per cent.	Approximate ratio.
1	30.09	32.94	36.97	$3BeO : SO_3 : 5H_2O$.
2	29.98	33.26	36.76	$3BeO : SO_3 : 5H_2O$.
3	21.00	44.50	34.50	$1.5\ BeO : SO_3 : 3.5\ H_2O$.
4	24.56	43.26	32.18	$1.8\ BeO : SO_3 : 3H_2O$.

The saturated sulphate is still slightly acid to litmus and has a slightly sweetish acid taste. It does not show any hydrolyzing action on sugar solution. In fact the H ions which are present to a slight extent in a solution of the normal sulphate (0.02 mol per mol of $BeSO_4$ in 0.2 molar solution) are thrown back long before the dibasic condition is reached. The soluble basic solutions are unaffected by dialysis.

INSOLUBLE BASIC SULPHATES.

If a sufficiently basic solution of beryllium sulphate is diluted with water, precipitates of much greater basicity than the dissolved sulphates are thrown out. The necessary amount of dilution depends upon the basicity. If the tribasic solution is used, there are three distinct precipitations, the different stages of which are probably more apparent than real, since the precipitates themselves vary little in composition. The point of the beginning of each precipitation and its end are not sharp, so that only very rough approximations of the necessary dilutions can be given, but the periods between the different precipitates where the further addition of water caused no apparent effect are prolonged and not to be mistaken. The extent to which this hydrolytic action proceeds is truly remarkable.

The two following experiments will lead to a better understanding of exactly what takes place. The tribasic solution used was prepared by adding an excess of basic beryllium carbonate to a 10 per cent. solution of the neutral sulphate or to a corresponding amount of sulphuric acid and evaporating on the water-bath. Under these conditions the carbonate is dissolved until the tribasic conditions are reached. At this point a reaction sets in between a part of the soluble tribasic sulphate and the remaining carbonate by means of which the latter loses all of its carbon

dioxide and forms a gum-like insoluble basic substance, of similar composition to those precipitated by water. The evaporation should not be carried too far, for if the solution becomes thick and syrupy it will be difficult to separate from the gummy residue and it can not be diluted. If this precaution is observed, the solution of the tribasic sulphate can be easily decanted from the residue.

(1) Three cc. of a syrupy solution, showing, on analysis, a ratio of $3BeO : SO_3$ was diluted with water at laboratory temperature. Precipitation was not permanent until about its own volume of water was added. Further addition of water threw down a voluminous white precipitate which momentarily appears gelatinous, but soon becomes snow-white and flocculent. Precipitation was complete before 50 cc. of water had been added. The precipitate was filtered, washed once and the solution further diluted without apparent effect to 400 cc., when it became milky, and on the further addition of water a second flocculent precipitate, resembling the first, but much less in amount, was thrown out. This second precipitate was washed once with a few cubic centimeters of water, the washings, as in the first instance, being added to the filtrate. Again on addition of pure water there was no apparent action until 1200 cc. in volume was attained when the solution again became slightly milky. This third precipitate does not easily gather together and, in fact, in repetition of this experiment it has not made itself manifest until the solution has stood some hours. On boiling down the solution the milkiness disappeared and was gradually replaced by a fine granular precipitate adhering firmly to the beaker, especially where it had been rubbed with a glass rod. To the unaided eye it exactly resembled ammonium magnesium phosphate, but under the microscope showed an entire lack of crystalline structure, as did also the first two precipitates. The relative quantities of beryllium oxide in each precipitate and of that left in solution were as follows:

	Per cent.
First precipitate	29.37
Second precipitate	7.63
Third precipitate	10.78
Left in solution	52.22

(2) Approximately 2 grams of a basic sulphate showing, by analysis, a ratio of $2.3BeO : SO_3$ was dissolved in water and di-

iuted. No precipitation whatever occurred until 50 cc. of water had been added, after which the precipitates came down in order as in the experiment already cited and, after the first, at about the same degree of dilution. The relative amounts of the beryllium oxide in each fraction were as follows:

	Per cent.
First precipitate	10.45
Second precipitate	5.37
Third precipitate	10.71
In solution	73.47

It will be seen at once that none of the residues left in solution after any precipitation could have been in the exact ratio of $2BeO : SO_3$.

The last precipitate being gathered together in large excess of water at the boiling temperature was more basic in character, even as high as 23 : 1, but was variable and differed little from the first two when they were subjected to the same treatment. Many analyses were made and the first two precipitates, when dried by pressure between filter-papers, also showed, on analysis, a variable composition. In no case was a basic ratio obtained as low as that given by Atterberg of 8 : 1. When freshly prepared they showed a ratio varying between 9 : 1 and 12 : 1, and the ratio was seldom one of whole numbers. On washing, they grew rapidly more basic in character and in one instance, a precipitate washed continuously for several weeks, reached a ratio as high as $35BeO : 1SO_3$. It appeared almost impossible, however, to remove the last traces of sulphuric anhydride by washing.

It was early apparent that the precipitates could not be separated from the mother-liquor for purposes of analysis and that it was by no means certain that a single basic salt or two different salts might not be present which were themselves decomposable by water. Fortunately the question can be settled by means of the phase-rule of Gibbs, and the conditions of its applicability to such problems as the identification of individuals in a mixture of basic salts with the mother-liquor have been most clearly pointed out by Miller and Kenrick,[1] and applied by Allen[2] and others.

In this case we have a system consisting of three components and if these have arrived at equilibrium at a fixed temperature and

[1] *Trans. Roy. Soc. of Canada*, **7**, III, 35.
[2] *Am. Chem. J.*, **25**, 308; **27**, 284.

pressure, the chances of having more than three phases (not considering the gaseous phase) are negligible. Thus in a series of experiments, if the mother-liquors have a constant concentration while the precipitates vary in composition when equilibrium is reached, then the precipitate is a mixture of two solid phases. If the mother-liquors vary in concentration while the precipitates have the same composition then the precipitate is a single chemical compound. If the precipitates and mother-liquors both vary in composition then the precipitate is a "solid solution," *i. e.*, a single solid phase of variable composition.

In order to study this question a series of experiments was carried out in a large, specially constructed thermostat, in which the solutions were agitated continuously in contact with the precipitates for several weeks at 25°. The experiment began on November 19, 1903, and the first samples of the mother-liquor were drawn for analysis on November 29th. Like samples were taken on December 7th and it being evident that equilibrium had been reached, all were sampled for analysis on December 10th. The thermostat was, however, kept running and on December 23rd further determinations were made which confirmed the previous condition of equilibrium. During the analyses it was noted that further precipitation took place on diluting the members of Groups III and IV, and in one or two instances in the other groups. It did not take place in Group V. The BeO and SO_3 are present in Groups I and II in the proportion of $3BeO : SO_3$; in Groups III and IV in the proportion of $2BeO : SO_3$; in Group V in the proportion of $6BeO : SO_3$; in Group VI in the proportion of $4BeO : SO_3$. The results follow:

		Taken.			Found.		
Group.	No.	Grams BeO.	Grams SO_3.	Grams H_2O.	Grams BeO in 10 cc. solution.	Grams SO_3 in 10 cc. solution.	Grams BeO / Grams SO_3 in solution.
	1	0.7560	0.3000	50	0.0802	0.1473	0.54
	2	1.1340	1.2000	50	0.1216	0.2147	0.57
I	3	1.5120	1.6000	50	0.1627	0.2844	0.57
	4	1.8900	2.0000	50	0.1995	0.3500	0.57
	5	2.2680	2.4000	50	0.2437	0.4193	0.58
	6	0.7560	0.8000	100	0.0382	0.0738	0.52
	7	1.1340	1.2000	100	0.0613	0.1142	0.53
II	8	1.5120	1.6000	100	0.0813	0.1457	0.56
	9	1.8900	2.0000	100	0.1014	0.1811	0.56
	10	2.2680	2.4000	100	0.1231	0.2132	0.58

Group.	No.	Taken. Grams BeO.	Grams SO_3.	Grams H_2O.	Found. Grams BeO in 10 cc. solution.	Grams SO_3 in 10 cc. solution.	Grams BeO / Grams SO_3 in solution.
	11	0.5040	0.8000	50	0.0943	0.1536	0.61
	12	0.7560	1.2000	50	0.1400	0.2269	0.61
III	13	1.0080	1.6000	50	0.1867	0.3002	0.60
	14	1.2600	2.0000	50	0.2293	0.3731	0.62
	15	1.5120	2.4000	50	0.2785	0.4622	0.60
	16	0.5040	0.8000	100	0.0462	0.0776	0.60
	17	0.7560	1.2000	100	0.0703	0.1159	0.61
IV	18	1.0080	1.6000	100	0.0942	0.1517	0.62
	19	1.2600	2.0000	100	0.1177	0.1925	0.61
	20	1.5120	2.4000	100	0.1394	0.2268	0.61
V	21	5.2920	2.8000	50	0.1710	0.4316	0.40
	22	5.2920	2.8000	100	0.0876	0.2241	0.39
VI	23	3.5280	2.8000	50	0.2360	0.4648	0.51
	24	3.5280	2.8000	100	0.1239	0.2432	0.51

A glance over the preceding figures will show at once that the concentrations of the mother-liquors vary widely and, therefore, the precipitates can not consist of a mixture of two definite basic salts. Other conclusions to be drawn are that an increase in the relative amount of BeO present diminishes the necessary amount of water to cause precipitation and also the basicity of the mother-liquors; that the concentration of the mother-liquors on equal dilution is directly proportional to the initial amount of the basic substance present and that a dilution from 50 to 100 cc., with the quantities present, does not appear to have caused further precipitation, since the ratio of base to acid is little, if any, changed. This last is in accord with the preliminary experiments and would seem to confirm the fact of the precipitation at different stages, which is difficult to understand. Further, a comparison of 1 and 11, 6 and 16, 21 and 23, and other corresponding numbers throughout shows that while an increase in the BeO present diminishes the ratio of BeO: SO_3 in solution it diminishes the total amount of SO_3, and in a greater relative proportion. This would tend toward similar composition for the precipitates, which is borne out by the results to follow.

It was hoped in the earlier stages of the work that the composition of the precipitates could be determined by calculations based on the amounts of material originally present and the amounts left in solution. This was found not possible from the facts that

the precipitates carried so little sulphuric anhydride, and in the case of Groups III and IV, while always present, were very small in amount. Consequently any error in the analyses of the portion of the solution taken, or in the determination of its fractional quantity, was many times multiplied in the calculation and made any conclusion as to the composition of the precipitates out of the question. The precipitates were, therefore, freed from the mother-liquors as completely as possible, were pressed between filter-paper so long as liquid was absorbed and were dried for several days to constant weight at 100° in air, free from carbon dioxide. The analyses of ten of these precipitates follow. The others were not analyzed, some being obtained in too small quantity for accurate work.

No.	BeO. Per cent.	SO_3. Per cent.	H_2O by difference. Per cent.
1	53.9	6.9	39.2
2	53.8	6.8	39.4
3	52.3	7.2	40.5
6	53.1	7.3	39.6
7	53.2	..	...
9	...	6.1	...
21	53.6	6.5	39.1
22	53.4	5.8	40.8
23	53.5	7.2	39.3
24	53.2	7.5	39.3

It will be seen at once that all of these precipitates contained notable quantities of sulphuric anhydride and much more than could be accounted for from any possible adhering mother-liquor. The presence of the small amount of mother-liquor introduces a slight unavoidable error, the effect of which is, however, to give a resultant solid less basic than the actual. The results themselves, taken literally, lead to formulas varying from $22Be(OH)_2.BeSO_4$ to $28Be(OH)_2.BeSO_4$, with a slight excess of water in every instance. The analyses are, however, subject to error and a slight error evidently has large effect in the calculation of such highly basic formulas. The possibility of the presence of two definite basic salts having been eliminated by the variation in concentration of the solutions, two propositions alone remain to us. First, that the precipitates are a single solid phase of definite composition which would prove the presence of a basic salt of a basicity of at least 25BeO to $1SO_3$, or that the precipitates vary in composition

and, therefore, are solid solutions containing a small amount of the sulphate in the hydroxide. In view of the well-known property of hydroxides to carry down other substances with them when precipitated and the utter improbability of any molecule of so large a ratio of base to acid, the latter conclusion seems justifiable.

I am pleased to acknowledge the efficient help of my assistant, Mr. H. B. Pulsifer, who did much of the analytical work and of Mr. M. A. Stewart, who determined the extent of hydrolysis of the normal sulphate in solution and the effect upon the amount of $\overset{+}{H}$ ions present obtained by saturating the same solution with its own carbonate.

The following conclusions seem warranted:

That the only known definite hydrated sulphates of beryllium are $BeSO_4 + 4H_2O$ and $BeSO_4 + 2H_2O$.

That the anhydrous sulphate $BeSO_4$ is difficult to produce entirely free from water or excess of oxide, owing to the difficulty of removing the last traces of water without at the same time driving off sulphuric anhydride.

That the so-called basic sulphates of beryllium do not exist as separate and definite chemical compounds, but are in reality solid solutions of the sulphate in the hydroxide. These are much more basic in composition when equilibrium with the mother-liquors is reached than when first precipitated.

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ON THE MOLECULAR DEPRESSION CONSTANT OF *p*-AZOXYANISOL.

BY H. MONMOUTH SMITH AND W. H. McCLELLAND.

Received August 1, 1904.

GATTERMANN and Ritschke[1] first prepared *p*-azoxyanisol and found that at 116° it passed into a turbid liquid of fluid crystals, which at 134° became a clear, transparent yellow liquid. Schenck,[2] in studying the compound, showed that both these transition points undergo abnormally large depressions, and from the depression of the "clear-turbid" transition point by seven

[1] *Ber. d. chem. Ges.*, **23**, 1738.
[2] *Ztschr. phys. Chem.*, **25**, 349.

solutes of various composition he calculated the molecular depression constant as 750.2. Later,[1] from determinations with eighteen solutes, he found values ranging from 503 to 859. Auwers[2] reported the value 545 as the average found by one of us[3] from determinations made with five solutes. In another series of determinations he reported[4] values ranging from 500 to 700.

Such a large depression constant is of special interest because of its size, and because, if it can be determined with accuracy, it will permit molecular weight determinations with the consumption of but a few milligrams of the solute. It seemed of interest then to redetermine this constant in the hope that more concordant results might be obtained.

The apparatus which was used in these experiments was of the usual Beckmann form, with a constant temperature bath of glycerol. The thermometer was divided into tenths of a degree and had been verified by the Reichsanstalt. The azoxyanisol was prepared according to the method of Lachman,[5] for azobenzene, and had transition points of 116° and 134°. The solutes were all of Kahlbaum's manufacture and gave sharp and constant melting-points.

Especial care was taken with reference to the conditions necessary to obtain uniform results and the following points may be mentioned:

(*a*) The glycerol bath must be at the highest possible temperature which will, at the same time, allow the formation of the fluid crystals. With the apparatus used in these experiments this limit was found to be from 2.5° to 3° above the transition temperature of the azoxyanisol. If the bath varied from this limit by a degree, the transition point was found from 0.5° to 1° too high.

(*b*) As a consequence of (*a*) it was found that any deviation whatever in the temperature of the bath during a determination gave discordant results which amounted to 4 per cent. for a temperature change in the bath of 0.5°.

(*c*) It was also noticed that the transition point of the freshly prepared azoxyanisol did not remain constant, but showed a grad-

[1] *Ztschr. phys. Chem.*, **29**, 554.
[2] *Ibid.*, **32**, 60.
[3] H. M. S.
[4] *Ztschr. phys., Chem.*, **42**, 631.
[5] This Journal, **24**, 1178.

ual rise during the first half-hour of heating, after which it became constant and remained so indefinitely.

The results of the determinations are given in Table I.

TABLE I.

Grams solvent.	Grams solute.	Observed depression.	Grams solute in 100 grams solvent.	Molecular depression constant, K.
	Naphthalene, molecular weight 128.			
8	0.0562	3.09	0.7025	561
8	0.1164	6.49	1.4550	570
8	0.1705	9.46	2.1310	566
			Average,	566
	α-Nitronaphthalene, molecular weight 173.			
8	0.0616	2.61	0.7700	586
8	0.1188	5.17	1.4840	601
8	0.1659	7.17	2.0737	598
			Average,	595
	Anthracene,[1] molecular weight 178.			
8	0.0586	2.20	0.7325	536
8	0.1311	4.61	1.6390	503
8	0.2021	7.14	2.5260	503
			Average,	514
	o-Acetotoluide, molecular weight 149.			
8	0.0627	3.51	0.7821	624
8	0.1207	6.69	1.5081	617
8	0.1626	9.26	2.0330	633
			Average,	625
	Acetamide,[1] molecular weight 59.			
8	0.0589	6.83	0.7362	546
8	0.0582	6.10	0.7275	495
			Average,	521
	p-Acetotoluide, molecular weight 149.			
8	0.0548	2.49	0.6844	542
8	0.1042	4.84	1.3020	554
8	0.1411	6.44	1.7640	544
			Average,	547
	Phenetol, molecular weight 122.			
8	0.0321	1.85	0.4006	564
8	0.0981	5.65	1.2250	567
8	0.2095	12.25	2.6130	572
			Average,	567
	Cinnamic acid, molecular weight 148.			
8	0.0515	2.59	0.6437	595
8	0.1147	5.47	1.4330	564
8	0.1606	7.31	2.0070	539
			Average,	566
		Grand average,	562.	

[1] Slightly volatile.

This average of 562 agrees better with that of 545, found by Auwers than with that found by Schenck.

Among the solutes used by Auwers[1] was benzil, which gave a value of 860 for the depression constant. This was so abnormal that it was not included by him in the average which he gave. On repeating this determination we obtained likewise an abnormal value which led us to try the action of three other bodies of ketone structure, the results of which are given in Table II.

TABLE II.

Grams solvent.	Grams solute.	Observed depression.	Grams solute in 100 grams solvent.	Molecular depression constant, K.
	Benzil, molecular weight 210.			
8	0.0571	2.80	0.7137	824
8	0.1310	6.20	1.6370	795
8	0.2014	9.81	2.5170	818
			Average,	812
	Benzoin, molecular weight 212.			
8	0.0619	3.52	0.7738	963
8	0.1176	6.83	1.4700	984
8	0.1714	9.64	2.1420	964
			Average,	967
	Benzophenone, molecular weight 182.			
8	0.0511	2.81	0.6387	802
8	0.1032	5.60	1.2890	790
8	0.1512	8.24	1.8900	793
			Average,	795
	Michler's ketone, molecular weight 168.			
8	0.0367	1.24	0.4587	723
8	0.0817	2.84	1.0200	745
8	0.1200	3.94	1.5000	705
			Average,	724
		Grand average,	825.	

The average of these four ketones gives a depression constant of 825, or 32 per cent. higher than that found by the eight substances in Table I.

The differences between the values heretofore found for the molecular depression constant have been attributed by Hulett[2] to the possible solubility of the solutes in the fluid crystals. Since

[1] *Ztschr. phys. Chem.*, **32**, 60.
[2] *Ibid.*, **28**, 642.

our determinations have been made, de Kock[1] has shown, in an exhaustive study of the subject, that such is the case, and that a small difference in the solubility coëfficients of the solutes in the two modifications of the solvent may produce variations in the depression constant. It appears then from the fairly uniform values in Table I that these substances have solubility coëfficients which do not differ widely, and for such substances azoxyanisol might be used in cryoscopic work, but it also appears from the results of the experiments with ketones, as given in Table II, that there are compounds which have large variations in the solubility coëfficients, and that it is these variations which are responsible for the differences in the molecular depression constant, and hence render cryoscopic work with azoxyanisol unreliable.

SYRACUSE UNIVERSITY,
June, 1904.

A CRITICISM OF CLARKE'S NEW LAW IN THERMOCHEMISTRY.[2]

BY H. E. PATTEN AND W. R. MOTT.

Received July 22, 1904.

A DISCUSSION of F. W. Clarke's paper, "A New Law in Thermochemistry," by W. v. Löben, appeared some time ago in the *Zeitschrift für anorganischen Chemie* (**34**, 175 (1903)), and in a later article Julius Thomsen stated his opinion that Clarke's results have no significance.

v. Löben maintains, and rightly, that Clarke has reasoned in a circle and that his constant is not a constant, since in the equation

$$\frac{4K}{12a + 6b - c - 8n} = \text{const.},$$

the different heats of combustion of isomers will change the value of K, while the denominator of that term takes no account of isomerism.

The authors of this paper look upon the work of Clarke as a painstaking and commendable attempt to reduce the data of ther-

[1] *Ztschr. phys. Chem.*, **48**, 151.

[2] A. A. Noyes, in his abstract of Clarke's paper (This Journal, **25**, R 256), suggests that possibly the choice of even integral numbers of henotherms to represent the various elementary heat effects may have brought about the agreement between the calculated and the observed heat effects as given by Clarke.

mal chemistry to an orderly system. It is true the method applied is that of assuming the constant first and working back from the above equation to a more exact value of the constant; it is true, too, that for derivatives of the hydrocarbons Clarke finds it necessary to introduce modifications into his formula to keep his constant constant. Further, it is evident that in choosing this constant upon which to build his equation Clarke took 13,700, because it is the value in thermal units attributed to the chemical affinity (or electrical strain) between hydrogen ions and hydroxyl ions. This arbitrary choice of the constant, 13,700, seems to us fortunate in that it enables one to test, along thermal lines, the validity of the conception that the affinity of elements and radicals for each other is the same and is independent of the individual element, dependent solely upon the number of valencies or atomic linkings involved; or, in terms of the ionic conception, dependent upon the number of electrical charges upon the ions in the reaction. Such a simplification would be welcome, if it accorded with the facts. It is evident that Clarke has neglected to consider the intensity factor which, of course, enters into the 13,700. On his basis the capacity factor is the same for all atoms or radicals, and this equivalence of the capacity factors of energy (coulombs) for different elements or radicals is the essence of Faraday's law of electrolysis. The fact that different voltages are required to decompose substances which take the same current is good evidence that all atomic linkings are not of the same thermal value.

A critical discussion of Clarke's mathematical work is given by v. Löben, as stated above. In addition we have represented graphically the deviations of Clarke's constant from a steady value and compared the heats of combustion as calculated by Clarke from his corrected constant "henotherm," with those obtained experimentally by Julius Thomsen.

The general type of the curves is shown in Plates I and II, the data for which were taken from Clarke's paper, "A New Law in Thermochemistry," pages 26 to 28. In general, the ordinates for the series of curves plotted by us are in per cent. variation of the calculated heat of combustion from the experimentally determined value; abscissae are usually CH_2 increments for the members of the ascending homologous series. Clarke's error is sometimes negative and sometimes positive, consequently we have plotted positive and negative values for his results. Thomsen's error being a true experimental error

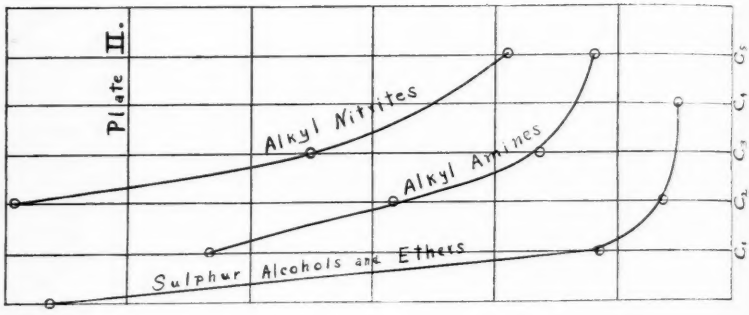
Plate II.
Alkyl Nitrites
Alkyl Amines
Sulphur Alcohols and Ethers
C1 C2 C3 C4 C5

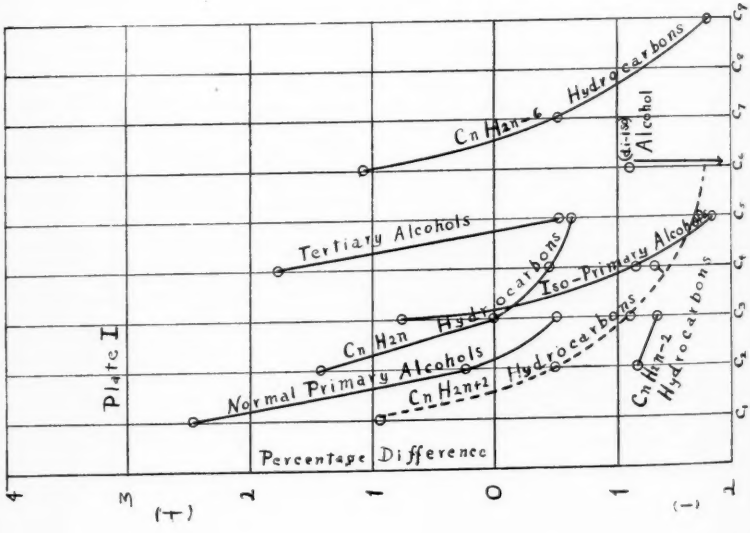
Plate I
Cn H2n-6 Hydrocarbons
Tertiary Alcohols
Cn H2n Hydrocarbons
Iso-Primary Alcohols
Normal Primary Alcohols
Cn H2n+2 Hydrocarbons
Cn H2n-2 Hydrocarbons
Alcohol
Percentage Difference
4 3 2 1 0 1 2
(+) (-)
C1 C2 C3 C4 C5 C6 C7 C8 C9

is likely to fall either positive or negative, and naturally becomes less and less as we ascend the series, since the total heat measured is greater on a gram-molecule of substance; therefore, we have plotted his curves in duplicate, using both the positive and negative ordinate with the same abscissae. In general, these curves show that Clarke's error starts well up on the positive ordinate for lower members of the homologous series where the carbon content is small and passes by a regular gradation, as we ascend the homologous series, through zero into the field of negative ordinates and becomes asymptotic to the axis of abscissa. This regularity of the curve of Clarke's error is observed in the paraffin, benzene and ethylene series for hydrocarbons, in the paraffin halides, alcohols, acids, amines, sulphur alcohols and sulphur ethers, and nitrites. The acetylene series, so far as studied, shows the same regularity for Clarke's error, although the curve lies entirely in the region of negative ordinates. The exceptional deviation of carbon tetrachloride from Clarke's law appears upon plotting the curve of his deviations for methane, methyl chloride, chloroform and carbon tetrachloride to be no exception at all, but rather exactly what is to be expected of a compound robbed of all four hydrogen atoms. A curve was roughly plotted by us from purely theoretical considerations, which shows that the diminution in the heat of combustion for members of an homologous series due to arbitrarily imagining one hydrogen atom to be removed from each member of the series forms a less and less per cent. of the total heat of combustion as we ascend the series. This is precisely the sort of regularity shown by the curves for Clarke's error. Such a regularity going through all classes of compounds considered by him shows, beyond question, that the deviations are not accidental or of the true experimental order of those of Thomsen, but are due to the CH_2 increment running throughout the series. Consequently, allowing Clarke all latitude as to his mathematical processes, he has not secured a constant thermal value for different atomic linkings. His so-called constant retains, mathematically concealed, the chemical differences in different organic compounds, and is really no more than recognizing that variation in physical properties in homologous series keeps pace with the CH_2 increment, a consideration not new.

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THE ACTION OF WATER UPON THE PHOSPHATES OF CALCIUM.[1]

By F. K. Cameron and A. Seidell.

Received August 18, 1904.

INTRODUCTION.

It has been shown by a number of investigators[2] that each of the three phosphates of calcium is decomposed or hydrolyzed by water. The dicalcium compound, however, at ordinary temperatures is decomposed to a much less extent than either of the others. The investigations which have so far been made on the action of water upon the phosphates of calcium were conducted, for the most part, under widely different conditions with respect to temperature, time of digestion, purity of product, etc. The experiments described in this paper were undertaken for the purpose of making a comparison of the decomposing action of water upon the three phosphates[3] under uniform conditions; and in addition, to obtain data upon the effect of some other calcium salts and of carbon dioxide upon the hydrolysis or decomposition which takes place. The calcium salts chosen are those most commonly present in the principal natural and artificial fertilizers. Their action upon the phosphates, which they accompany, is not clearly understood, although a great many important observations upon the subject have been made.

Tricalcium phosphate, prepared by precipitation, is non-crystalline, and a reasonably pure and crystalline product, with well defined characteristics of a definite molecular species, has not been prepared. It is significant that crystallized tricalcium phosphate does not itself occur in nature,[4] but only as a mixture or in combination with other substances.

Both monocalcium and dicalcium phosphates (or their hydrates) separate in crystalline form as definite, well characterized compounds, from solutions containing an excess of phosphoric

[1] Published by permission of the Secretary of Agriculture.

[2] For references see this Journal, **26**, 885 (1904).

[3] The occurrence of the so-called tetracalcium phosphate, $Ca_4P_2O_9$, in practically pure condition as crystals in a slag has been observed by Otto (*Chem. Ztg.*, **18**, 255 (1887)) and, mixed with other substances, by several observers, *vide*, Wiley and Krug (*J. Anal. Chem.*, **5**, 685 (1891)), but it does not appear to have been recognized as formed in the wet way, and, therefore, need not be further considered here.

[4] Vide, Groth: *Tabellarische Übersicht der Mineralien*, p. 71: "Dasselbe gilt —— in dem als Hauptsbestandtheil wohl das normale Calciumphosphat $(PO_4)_2Ca_3$ auzunehmen ist, welches man bisher in der Natur noch nicht in reinem Zustande kennt; würde dasselbe regular krystallizirt, so wäre ——."

acid. It has been frequently observed that monocalcium phosphate is, in part at least, decomposed in water, and that in general the extent of the decomposition depends upon the proportion of water to solid phosphate.[1] Judging from the statements in the literature, dihydrate of dicalcium phosphate is the compound which, at ordinary temperatures and conditions, is the stable one over the widest range of concentration of the supernatant acid solution. Rindell,[2] however, observed that this substance was slightly decomposed by water.

The phosphates used in this investigation were obtained in original sealed packages from Kahlbaum. The tricalcium compound was a white powder in which no crystalline structure could be detected by a microscopical examination. The dicalcium compound was finely powdered, but remnants of crystals were readily detected by the microscope, and the monocalcium compound was in small but well-formed crystals. While it was certain that these samples were reasonably free from other contaminations, they were all found to contain more phosphoric acid than would be required by the respective formulas for tri-, di- or monocalcium phosphate. While this detracts from the value of the data obtained from the point of view of absolute measurements, it cannot be regarded as materially affecting the significance of the results for demonstrating the nature of the reaction between the several phosphates and water. From their nature it is impracticable to obtain tri- or monocalcium phosphate free from an excess of either base or acid, and consequently the absolute values of the solubility effects are of minor importance as compared with the order of magnitude and general direction of the effects.

In order to obtain uniformity all of the solutions were prepared at the same time, as nearly as practicable, by weighing into 8-ounce sterilizer bottles the desired amounts of the phosphate and the other calcium salts. In every case 200 cc. of distilled water were added. The bottles were kept in a large water-bath maintained at 25° C., but were removed at intervals and shaken by hand. The bottles containing the solutions which were treated with carbon dioxide were taken from the bath at each introduction of the gas and a rapid stream of it passed through the solutions for one minute.

[1] Stoklasa · *Listy Chem.*, **13**, 203, 240, 273. Abstract *J. Chem. Soc.*, **58**, 695 (1890). The original papers are not accessible to us.

[2] *Compt. Rend.*, **134**, 112 (1902).

There were three series of 24 bottles each, corresponding to the tri-, di- and monocalcium phosphate respectively. The bottles in each series formed two groups of twelve each, identical in all respects save the presence of carbon dioxide in one group of each series and its absence from the other. The bottles were withdrawn from the constant temperature bath in groups and aliquot portions of the clear solutions taken for analysis.

All figures in the tables are in grams per liter. No correction for water or adhering acid was made in weighing the original phosphates.

Tricalcium Phosphate.—Warington[1] showed that tricalcium phosphate containing slightly more calcium than required by the formula was decomposed by boiling in water for two hours to such an extent that the solution contained about three times as much phosphoric acid as calcium. The decomposing action was possessed to a lesser extent by cold water. He also found that the amount of phosphoric acid which water would extract depended on the relative masses of the phosphate and water that are brought together. These observations have been verified by the experiments described in a recent paper from this laboratory. The material which was used in the experiments there recorded contain, like Warington's, a slight excess of calcium. The analysis of the material showed it to correspond to 85.07 per cent. calcium phosphate, $Ca_3(PO_4)_2$, 0.14 per cent. calcium hydroxide, $Ca(OH)_2$, and 14.69 per cent. moisture.

The material used for the experiments recorded in the present paper corresponded to 87.22 per cent. calcium phosphate, $Ca_3(PO_4)_2$, 2.83 per cent. phosphoric acid, H_3PO_4, and 9.98 per cent. moisture. A comparison of the results obtained with the two compounds is given in Table I, the figures for the compound containing an excess of calcium being interpolated from results already published. These figures not only show that the nature of the particular product used determined the composition of the solution and that the phosphate which originally contained the larger proportion of phosphoric acid yielded the more acid to the solution, but an inspection of the figures brings out the important fact that in the last series the amount of phosphoric acid, PO_4, entering solution is less than would be expected from the excess of acid in the original phosphate above that required by the formula $Ca_3(PO_4)_2$.

[1] *J. Chem. Soc.*, **26**, 983 (1873).

TABLE I.

Grams phosphate per liter.	Grams PO_4 dissolved per liter. Sample containing an excess of Ca.	Sample containing an excess of PO_4.
5	0.068	0.109
10	0.113	0.189
20	0.185	0.324
40	0.310	0.558

From these results it is apparent that all determinations of the solubility of tricalcium phosphate, which have so far been made, are open to objection. The products which have been used vary among themselves, according to their source and preparation, to as great, if not a greater, extent than the samples which were used for the preceding experiments, and the absolute values of the results obtained can, therefore, have very little value as physical constants.

The results of the analyses of the series of solutions prepared with the Kahlbaum tricalcium phosphate, together with calcium sulphate or calcium carbonate and without, in distilled water previously boiled to eliminate dissolved carbon dioxide and then cooled rapidly, and in distilled water containing carbon dioxide, are given in Table II.

TABLE II.—ACTION OF WATER AND SOLUTIONS UPON TRICALCIUM PHOSPHATE. TIME OF CONTACT, THIRTY-FIVE DAYS.

Grams $Ca_3(PO_4)_2$ per liter.	Without CO_2. Grams per liter of Ca.	Without CO_2. Grams per liter of PO_4.	With CO_2. Grams per liter of Ca.	With CO_2. Grams per liter of PO_4.
	With water alone.			
5	0.014	0.109	0.085	0.239
10	0.019	0.189	0.114	0.344
20	0.031	0.324	0.114	0.481
40	0.050	0.558	0.134	0.738
	In contact with solid calcium sulphate.			
5	0.620	0.113	0.646	0.217
10	0.640	0.205	0.659	0.315
20	0.644	0.360	0.662	0.451
40	0.666	0.623	0.682	0.715
	In contact with solid calcium carbonate.			
5	0.034	trace	0.352	trace
10	0.073	"	0.354	"
20	0.106	"	0.327	"
40	0.134	"	0.306	"

The average of sulphate determinations for the saturated calcium sulphate solutions gave 2.087 grams $CaSO_4$ per liter of solution without CO_2, and 2.029 grams $CaSO_4$ per liter of solution with CO_2. The calcium determinations as given in the above table for these solutions are to be corrected for 0.614 and 0.597 gram Ca, dissolved as calcium sulphate in the solutions free from and containing carbon dioxide, respectively, in order to obtain the amounts of calcium which were dissolved as phosphate.

The results contained in Table II show, in general, the direction of the changes in the decomposition or hydrolysis of tricalcium phosphate produced by the two calcium salts and carbon dioxide. It is seen that calcium sulphate augments the decomposition when no carbon dioxide is present; slightly decreases it when carbon dioxide is present, while calcium carbonate retards it. Carbon dioxide increases the amount of PO_4 dissolved in the solutions of water alone and the saturated calcium sulphate solutions, but has no other effect than to increase the amount of calcium in the solutions in contact with calcium carbonate. It appears that solutions of neither calcium carbonate nor bicarbonate have any marked solvent or decomposing action upon the calcium phosphate.

Georgievics[1] studied the action of carbon dioxide on tricalcium phosphate. He experimented with quantities of material only one-tenth as large, per liter of water, as used in the work here described. He concluded that tricalcium phosphate is transformed into dicalcium phosphate and dissolved as such in solutions treated with a slow stream of carbon dioxide for twenty-four to forty-eight hours, but he also states that tricalcium phosphate dissolves as such in solutions of calcium bicarbonate.

An examination of the figures in Table II will show that the ratio of the reacting weight of calcium to that of phosphoric acid in solution steadily increases with increase of the mass of solid phosphate, and does not remain constant. Georgievics was probably misled, on account of the small quantities of solid phosphate he used producing but slight differences in the solutions, into thinking this ratio was constant and approximately that required by the formula for dicalcium phosphate. Only traces of phosphoric acid were found in the solutions containing calcium bicarbonate, which invalidates Georgievics' further assumption that under such circumstances tricalcium phosphate dissolves as such.

[1] *Monatsh. für Chem.*, **12**, 566 (1891).

Dicalcium Phosphate.—The action of water on dicalcium phosphate has recently been investigated by Rindell,[1] who employed a product having a composition closely approximating that represented by the formula $CaHPO_4.2H_2O$. He found that the ratio of the quantities of lime and phosphoric acid dissolved is practically constant and independent of the relative amounts of solid and solvent used. This ratio, however, in molecular quantities, as calculated from Rindell's results, was 1.68 instead of unity, indicating that when hydrated dicalcium phosphate is subjected to the action of water a decomposition takes place, and that a condition of equilibrium is reached, the solution containing an excess of phosphoric acid.

The sample of dicalcium phosphate used for the experiments, described in this paper, gave, on analysis, Ca 29.06 per cent., PO_4 70.84 per cent., corresponding to 98.71 per cent. dicalcium phosphate and 1.23 per cent. phosphoric acid. The results presented in Table III for the solutions of this product in water alone show, as do Rindell's, that the amount of calcium and phosphoric acid dissolved is practically independent of the proportion of phosphate to water used. The ratio of the molecular quantities of calcium, Ca, to phosphoric acid, PO_4, dissolved is, however, 1.32 instead of 1.68, as found by Rindell.

The difference in the molecular ratios of the calcium to phosphoric acid in solution in the two cases is probably due to the nature of the sample employed. In the latter case an excess of phosphoric acid above that necessary to combine with the calcium was shown by the analysis to be present. One might, therefore, expect the ratio in this latter case to be the larger, whereas, actually, it was less.

The results of the experiments upon the conduct of dicalcium phosphate in contact with pure water and when in contact with an excess of calcium sulphate, or calcium carbonate, as well as similar solutions treated with carbon dioxide, are given in Table III.

The average of sulphate determinations in the saturated calcium sulphate solutions gave 2.108 grams $CaSO_4$ per liter of solution without CO_2, and 1.941 grams $CaSO_4$ per liter of solution with CO_2. The calcium determinations as given are to be corrected for 0.620 and 0.571 gram of calcium dissolved as calcium sul-

[1] *Compt. Rend.*, **134**, 112 (1902).

TABLE III.—ACTION OF WATER AND SOLUTIONS UPON DICALCIUM PHOSPHATE. TIME OF CONTACT, THIRTY-EIGHT DAYS.

Grams $CaHPO_4$ per liter.	Without CO_2. Grams per liter of		With CO_2. Grams per liter of	
	Ca.	PO_4.	Ca.	PO_4.
	With water alone.			
5	0.039	0.090	0.169	0.392
10	0.033	0.116	0.160	0.388
20	0.036	0.117	0.162	0.395
40	0.039	0.131	0.166	0.402
	In contact with solid calcium sulphate.			
5	0.619	0.016	0.683	0.299
10	0.624	0.016	0.690	0.306
20	0.612	0.040	0.687	0.281
40	0.636	0.064	0.687	0.299
	In contact with solid calcium carbonate.			
5	0.110	0.037	0.291	0.084
10	0.110	0.043	0.284	0.089
20	0.119	0.043	0.289	0.080
40	0.120	0.045	0.313	0.081

phate in the solutions free from and containing carbon dioxide, respectively. It is interesting to observe the effect here of the phosphate in decreasing the solubility of the calcium sulphate.

The results in Table III show that, with the possible exception of the saturated calcium sulphate solutions, the decomposition of the dicalcium phosphate depends but slightly upon the relative amounts of solid and solvent which are present. In all cases the addition of carbon dioxide to the solutions has resulted in an increase in the decomposition. The presence of calcium sulphate, as well as of calcium carbonate, decreased the amount of phosphoric acid which dissolved. In the case of the saturated calcium sulphate solutions not treated with carbon dioxide the calcium in solution was only equivalent to that required by the sulphate dissolved. In the solutions treated with carbon dioxide, however, the amount of calcium present was more, and was probably dissolved either as phosphate or bicarbonate. It is to be noted that the calcium sulphate in the solutions treated with carbon dioxide was less than in the solutions not so treated. It, therefore, appears that the solubility of the calcium sulphate itself was decreased by the other calcium salts present.

With regard to the solutions in contact with calcium carbonate it will be observed that in the solutions not treated with carbon dioxide more phosphoric acid was present than in the similar solutions in contact with calcium sulphate. In the solutions treated with carbon dioxide, however, less phosphoric acid was dissolved than in the similar solutions in contact with calcium sulphate. It follows, therefore, that calcium hydrogen carbonate solutions have a more marked action on dicalcium phosphate than do solutions of calcium sulphate alone, but calcium sulphate and carbon dioxide together decompose a larger quantity of phosphate than either of the calcium salts separately.

Monocalcium Phosphate.—It has been stated by Stoklasa[1] that monocalcium phosphate itself is not hygroscopic, but that the hygroscopic nature of the usual preparation is due to free phosphoric acid, which is almost always present. Stoklasa treated preparations of monocalcium phosphate with varying quantities of water. The original papers are not accessible to us, however, and a comparison can not be made of the results obtained by him with those obtained in this investigation.

The preparation which was used for the work described in this paper was well crystallized, but evidently contained free phosphoric acid in considerable excess, as shown by the following analysis: Ca found, 15.17 per cent.; $CaH_4(PO_4)$ calculated from Ca found, 88.67 per cent.; PO_4 calculated from Ca found, 71.88 per cent.; PO_4 found, 79.58 per cent.

On account of its greater solubility it was necessary to use larger proportions of the monocalcium phosphate than of the other phosphates to the usual volume of water in order to obtain the solutions in contact with the solid phosphate. The results which were obtained by digesting different quantities of the salt in water and in solutions in contact with solid calcium sulphate are given in Table IV.

TABLE IV.—ACTION OF WATER AND SOLUTION OF CALCIUM SULPHATE UPON MONOCALCIUM PHOSPHATE.

Grams $CaH_4(PO_4)_2$ per liter.	With water alone. Grams per liter of		With solid $CaSO_4$. Grams per liter of	
	Ca.	PO_4.	Ca.	PO_4.
40	0.534	29.85	0.572	30.38
80	0.920	54.98	1.051	56.58
120	1.375	84.04	1.463	84.30
160	1.692	105.50	1.797	106.02

[1] *Loc. cit.*

From these data it appears that monocalcium phosphate is greatly decomposed by water, and that the resulting solution is to be regarded as a solution of the decomposition products rather than of the substance itself. The presence of an excess of calcium sulphate does not materially affect the amount of phosphoric acid entering the solution, the slight discrepancies appearing in the table being due much more probably to experimental errors than to real differences. A similar set of solutions was also treated with calcium carbonate in the proportion of 10 grams of the carbonate to a liter of solution with the result that the carbonate was entirely dissolved and the phosphoric acid in solution and the acidity of the solutions were reduced in amounts practically equivalent to the added calcium carbonate. The results are not given, since they show nothing further regarding the action of the solutions.

Duplicate sets of all these solutions were treated repeatedly with carbon dioxide, but the treatment in no case produced any appreciable effect upon the phosphoric acid nor calcium dissolved, nor upon the acidity of the resulting solution and it does not seem worth while to present the results here.

SUMMARY.

From the foregoing data it appears that tricalcium phosphate and monocalcium phosphate are alike in their conduct towards water in that both are very much hydrolyzed and decomposed. With tricalcium phosphate, former study in this laboratory makes it appear improbable that final equilibrium conditions were obtained in the work here described, but with the monocalcium phosphate there can be but little doubt that the results here given do represent final conditions, and that it is safe to say that with both tri- and monocalcium phosphate the amount of decomposition and the concentration of the resulting solution at the temperature employed is dependent upon the proportion of the mass of solid phosphate to the mass of water.[1]

Dicalcium phosphate is unlike the mono- and tri-compounds, in that it is, relatively speaking, but slightly decomposed by water, and appears to dissolve mainly as such. In other words, it is the only phosphate of calcium which is stable in water under ordinary conditions.

[1] A systematic study of the concentrations of phosphoric acid which condition equilibrium between solution and mono- and dicalcium phosphate as stable solid phases is now in progress.

The presence of calcium sulphate slightly increases the phosphoric acid dissolved from tricalcium phosphate, produces probably a slight increase with monocalcium phosphate, but a marked decrease with dicalcium phosphate.

The presence of calcium carbonate decreases the phosphoric acid dissolved from all three phosphates.

Carbon dioxide increases the phosphoric acid dissolved from tri- or dicalcium phosphate, but does not appear to affect the action of water upon monocalcium phosphate.

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THE COLORIMETRIC ESTIMATION OF PHOSPHATES; SECOND METHOD.[1]

BY OSWALD SCHREINER AND BAILEY E. BROWN.

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THE estimation of small amounts of water-soluble phosphates has within the past few years become a matter of considerable interest in sanitary, physiological, and agricultural chemistry, as well as in physico-chemical studies on slightly soluble phosphates. The small amounts available for analysis in many cases led to the adoption of colorimetric instead of gravimetric methods. Quite a number of procedures have been devised during the past few years,[2] but all have as a basis the development of the yellow color of the phosphomolybdates in acid solution. This phosphomolybdate coloration is influenced somewhat by the presence of larger quantities of other salts, but the chief difficulty lies in the similar and even more intensive coloration produced by the silicomolybdates. The chief aim in the various proposed procedures has been the elimination of the color produced by these silicomolybdates, either by eliminating the silica itself or by means of a differential coloration of the solutions by varying the procedure. Another difficulty met with in dealing with the natural solutions is the disturbing influence of foreign organic coloring-matter. It has, therefore, always been necessary to completely decolorize the solution before proceeding with the colorimetric test.

[1] Published by permission of the Secretary of Agriculture.

[2] See West-Knights: *Analyst*, **5**, 197 (1880); Lepierre: *Bull. Soc. Chim.* (3), **15**, 1213 (1896); Jolles and Neurath: *Monatsh. Chem.*, **19**, 5 (1898); Jolles: *Arch. f. Hygiene*, **34**, 22 (1899); Woodman and Cayvan: This Journal, **23**, 96 (1901); Woodman: *Ibid.*, **24**, 735 (1902); Veitch: *Ibid.*, **25**, 169 (1903); Schreiner: *Ibid.*, **25**, 1056 (1903); **26**, 808 (1904).

In a recent paper on the colorimetric estimation of magnesium[1] it was shown that very small quantities of magnesium could be precipitated as magnesium ammonium phosphate, washed with ammonia water and then dissolved in nitric acid and the phosphoric acid estimated by the well-known phosphomolybdate colorimetric methods referred to above. This work has been continued in the laboratory of soil chemistry, especially in its application to the estimation of phosphates. It was but natural to try the reverse of the magnesium procedure, that is, to add a magnesia reagent to a solution of a phosphate and thus precipitate the phosphate in the form of magnesium ammonium phosphate, and by washing get rid of all silica, organic coloring-matter, as well as perhaps other salts, the presence of which would influence the phosphomolybdate coloration. The results of this test is given in Table I. In the first two columns the actual amount of P_2O_5 used in making the test is given, and in the last two columns the parts of P_2O_5 per million of solution.

TABLE I.—PRELIMINARY TEST.

Milligrams P_2O_5.		Parts P_2O_5 per million of solution.	
Present.	Found.	Present.	Found.
0.625	0.621	12.50	12.42
0.625	0.625	12.50	12.50
0.625	0.600	12.50	12.00
0.625	0.637	12.50	12.74

A more extended series of solutions of phosphates, as well as solutions containing the silicates, sulphates, chlorides and nitrates of sodium, potassium, calcium and magnesium, was then made with equally good results, as will be shown. In the colorimetric magnesium method the calcium was removed by precipitation with ammonium oxalate. It appeared to be safest to follow this same procedure in the present method, although the necessity is not so apparent.

METHOD FOR DETERMINING PHOSPHATES COLORIMETRICALLY.

The following reagents will be required:

(1) *Ammonium Molybdate Solution.*—Fifty grams of the pure salt in 1 liter of solution.

(2) *Nitric Acid.*—Specific gravity 1.07.

(3) *Standard Phosphate Solution.*—0.5045 gram of pure freshly crystallized sodium phosphate, $Na_2HPO_4.12H_2O$, is dissolved in

[1] This Journal, **26**, 961 (1904).

water, 100 cc. of nitric acid (sp. gr. 1.07) added, and the whole diluted to 1 liter. The nitric acid is added to lessen the contamination with silica from the glass. One cc. = 0.0001 gram P_2O_5.

(4) *Standard Colorimetric Solution.*—This is prepared by diluting 10 cc. of the standard phosphate solution (3) to about 80 cc. and then adding 9 cc. of nitric acid (2), 8 cc. of ammonium molybdate solution (1), and making up to 100 cc. After standing twenty minutes it is ready for use. Each cubic centimeter of this colorimetric solution is equal to 0.00001 gram P_2O_5.

(5) *Ammonium Hydroxide.*—Reagent.

(6) *Ammonium Hydroxide Wash Liquid.*—One part of strong ammonia water (sp. gr. 0.9) and 9 parts of water. This liquid should be practically free from silica, and for this reason is best prepared from redistilled ammonia water.

(7) *Ammonium Oxalate.*—Saturated solution.

(8) *Magnesia Reagent.*—Dissolve 13 grams of magnesium chloride, $MgCl_2.6H_2O$, and 20 grams of ammonium chloride, NH_4Cl, in about 900 cc. of water, add 50 cc. of strong ammonia water (sp. gr. 0.9) and dilute to 1 liter. One cc. of this solution will precipitate 3.5 mg. of P_2O_5.

(9) *Filter-paper.*—This must be free from silica. Schleicher and Schüll's No. 589 or 590, 7 cm. has been found to be very satisfactory for this colorimetric work.

The colorimeter used in these tests was the same as the second instrument described briefly in the earlier paper on the colorimetric estimation of magnesium.

The procedure for the method is as follows: Measure out a convenient volume of the solution to be estimated, usually 50 cc., into an evaporating dish, add 1 drop of ammonia water (5), and 2 or 3 drops of the ammonium oxalate solution (7); evaporate to dryness on a water-bath. To the cooled dish add 1 cc. of the magnesia reagent (8) work up the residue well with a glass rod and then allow to stand about two hours. The precipitated magnesium ammonium phosphate is then washed as follows: Add about 5 cc. of the ammonium hydroxide wash-liquid (6) to the dish, washing down the sides, and then pour the liquid through a small filter (9). Repeat this operation five times, then wash down the filter and funnel until the filtrate measures approximately 50 cc.; then rinse the dish once with about 5 cc. of cold water,

and pour through the filter in such a way as to wash the filter; reject the washings and put a clean salt mouth bottle or other receptacle under the funnel. Add 5 cc. of nitric acid (2) to the dish, working this about with the glass rod and pour through the funnel in such a manner as to wet all the inside of the funnel; then wash the dish five times with hot water (about 5 cc. each) and continue washing the filter until about 45 cc. of the filtrate have been obtained. To the cooled liquid add 4 cc. of the ammonium molybdate solution (1) and, after twenty minutes, read against the standard colorimetric phosphate solution (4).

The remarks on the development of the color and handling of the solutions given in the earlier papers cited naturally apply also in the present instance. As mentioned above, the ammonia wash-liquid should be practically free from silica, which end is readily attained by distillation. If old ammonia water containing considerable silica is used, the single last washing with pure water will not, of course, remove all of the silica from the filter-paper, and the results will be erroneous.

In Table II a series of results obtained with solutions of varying concentrations of phosphates is given. The first two columns give the actual amounts worked with, the second two the parts per million of solution.

TABLE II.—TESTS ON SOLUTIONS OF PHOSPHATES.

Milligrams P_2O_5.		Parts P_2O_5 per million of solution.	
Present.	Found.	Present.	Found.
1.250	1.245	25.00	24.90
1.250	1.235	25.00	24.70
1.250	1.250	25.00	25.00
1.000	1.010	20.00	20.20
1.000	1.010	20.00	20.20
0.750	0.775	15.00	15.50
0.750	0.755	15.00	15.10
0.625	0.620	12.50	12.40
0.625	0.624	12.50	12.48
0.625	0.618	12.50	12.36
0.625	0.621	12.50	12.42
0.500	0.507	10.00	10.14
0.500	0.514	10.00	10.28
0.500	0.508	10.00	10.16
0.500	0.500	10.00	10.00
0.375	0.373	7.50	7.46
0.375	0.387	7.50	7.74

TABLE II.—(*Continued.*)

Milligrams P_2O_5.		Parts P_2O_5 per million of solution.	
Present.	Found.	Present.	Found.
0.313	0.311	6.26	6.22
0.313	0.312	6.26	6.24
0.250	0.250	5.00	5.00
0.250	(0.300)	5.00	(6.00)
0.250	0.250	5.00	5.00
0.250	0.248	5.00	4.96
0.250	0.248	5.00	4.96
0.250	0.256	5.00	5.12
0.250	0.252	5.00	5.04
0.200	0.203	4.00	4.06
0.200	0.198	4.00	3.96
0.150	0.155	3.00	3.10
0.150	0.153	3.00	3.06
0.125	0.124	2.50	2.48
0.125	0.132	2.50	2.64
0.125	0.131	2.50	2.62
0.100	0.105	2.00	2.10
0.100	0.108	2.00	2.16
0.063	0.064	1.26	1.28
0.050	0.055	1.00	1.10
0.050	0.054	1.00	1.08

An examination of the results shows them to be quite satisfactory for such small quantities. All the results are fully within one part per million of solution, except the twenty-first result, in parenthesis, where six parts per million were found when only five parts were present.

The influence of other salts, and more especially silicates, was tried by making solutions of varying amounts of phosphates and constant amounts of the silicates, sulphates, chlorides and nitrates of sodium, potassium, calcium and magnesium. The concentration of these substances in the solutions was approximately as follows:

	Parts per million.		Parts per million.
Mg	10.0	SO_4	40.0
Ca	10.0	Cl	20.0
K	10.0	NO_3	15.0
Na	5.0	SiO_2	10.0

Total salts = 120 parts per million of solution.

The results obtained with these solutions are given in Table III.

TABLE III.—TESTS ON SOLUTIONS OF PHOSPHATES CONTAINING ALSO SILICATES, SULPHATES, CHLORIDES, AND NITRATES OF SODIUM, POTASSIUM, CALCIUM, AND MAGNESIUM.

Milligrams P_2O_5.		Parts P_2O_5 per million of solution.	
Present.	Found.	Present.	Found.
1.250	1.215	25.00	24.30
1.250	1.210	25.00	24.20
1.000	1.020	20.00	20.40
1.000	1.005	20.00	20.10
0.750	0.775	15.00	15.50
0.750	0.762	15.00	15.24
0.625	0.614	12.50	12.28
0.625	0.630	12.50	12.60
0.500	0.510	10.00	10.20
0.500	0.512	10.00	10.24
0.500	0.500	10.00	10.00
0.500	0.504	10.00	10.08
0.375	0.383	7.50	7.66
0.375	0.385	7.50	7.70
0.250	0.248	5.00	4.96
0.250	0.255	5.00	5.10
0.250	0.270	5.00	5.40
0.250	0.252	5.00	5.04
0.250	0.267	5.00	5.34
0.250	0.283	5.00	5.66
0.200	0.203	4.00	4.06
0.200	0.222	4.00	4.44
0.150	0.150	3.00	3.00
0.150	0.162	3.00	3.24
0.125	0.144	2.50	2.88
0.125	0.155	2.50	3.10
0.100	0.121	2.00	2.42
0.100	0.113	2.00	2.26
0.050	0.097	1.00	1.94
0.050	0.072	1.00	1.44

This method has several advantages: (1) It is based on the same procedure as that followed in gravimetric work; (2) all other salts, including silicates, are completely removed and the phosphomolybdate color is, therefore, developed in a solution free from disturbing factors; (3) the presence of coloring-matter in the original solution does not influence the result, as it is entirely removed or destroyed during the procedure. The method has shown itself to be quite rapid and, as with the magnesium method, proper attention to details will enable one man to make twenty to twenty-five determinations in a working day of seven hours.

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[Contribution from the Havemeyer Laboratories of Columbia University, No. 101].

THE DETERMINATION OF NITROGEN IN ORGANIC COMPOUNDS.

By H. C. Sherman and M. J. Falk.

Received September 3, 1904.

The Kjeldahl method of decomposing organic matter by digestion with strong sulphuric acid having been subjected to so many modifications, a series of comparative determinations was undertaken to find, if possible, the most advantageous form of the process and to test its applicability to different types of organic substances. The results of the work upon food materials and physiological products were recently published.[1] A similar study with a few other natural products and some pure compounds has since been concluded.

The digestion of the sample with sulphuric acid was carried out in different ways, the usual method of distillation being used throughout. Usually 0.5 or 1 gram[2] of the substance, according to its nitrogen content, was taken for each determination and transferred to the flask by means of pure filter-paper. About 0.5 gram of cellulose was thus introduced with the sample.

The methods of digestion, compared in the series with pure compounds, were:

(1) The Kjeldahl-Willfarth method as adopted by the Association of Official Agricultural Chemists.[3] The sample was treated with sulphuric acid and mercury, boiled until colorless and potassium permanganate added in small portions until the solution remained permanently colored.

(2) As in (1), except that the potassium permanganate was omitted.

(3) As in (2), except that the boiling was continued for two hours after the liquid had become colorless.

(4) The Gunning process as adopted by the Association of Official Agricultural Chemists.[4] About 20 cc. of sulphuric acid and 10 grams of potassium sulphate were used and the boiling continued until the solution became colorless.

(5) As in (4), but boiled two hours longer.

[1] This Journal, **26**, 367.

[2] Of the peppers and tobacco mentioned below, portions of 1 to 2 grams were taken.

[3] U. S. Dept. Agr., Bureau of Chemistry, Bull. 46.

[4] *Loc. cit.*

PERCENTAGES OF NITROGEN FOUND BY MODIFICATIONS OF KJELDAHL METHOD.

		WILLFARTH MODIFICATION. Boiled till colorless.				GUNNING MODIFICATION. Boiled till colorless.			DYER MODIFICATION. Boiled till colorless.			
Substance.	Theoretical.	Time of boiling. Hrs. Min.	$KMnO_4$ used. (1)[1].	$KMnO_4$ omitted. (2).	Boiled 2 hours longer. (3).	Time of boiling. Hrs. Min.	(4).	Boiled 2 hours longer. (5).	Time of boiling. Hrs. Min.	(6).	Boiled ½ hour longer. (7).	Boiled 2 hours longer. (8).
Benzamide	11.59	3 : 0	11.57	11.41	11.50	4 : 0	11.45	11.54	1 : 0	11.54	11.58	11.58
Betaine hydrochloride	9.15	1 : 0	7.11 9.02	6.20	8.92	1 : 0	9.11	9.13	0 : 15	7.42	9.12	....
Acetanilide	10.32	1 : 35	10.14	10.04	10.19	1 : 45	10.11	10.24	0 : 50	10.07	10.31	10.31
Naphthylamine	9.80	3 : 40	9.45	9.38	9.49	2 : 20	9.57	9.62	0 : 40	9.66	9.74	9.75
Diphenylamine	8.30	2 : 30	7.85	7.66	7.76	3 : 0	7.74	7.84	0 : 45	7.75	8.30	8.32
Cinchonine sulphate	7.75	1 : 00	7.64	5.00	7.56	2 : 15	6.65	6.91	0 : 30	6.03	6.57	7.65

[1] The number in parenthesis at the head of each column is that of the method, outlined above, by which the percentages of nitrogen shown in that column were found.

(6) The Dyer modification[1] of Gunning's method. The substance was heated with sulphuric acid and mercury until frothing subsided, after which 10 grams potassium sulphate were added and the solution boiled until colorless.

(7) As in (6), but boiled one-half hour after colorless.

(8) As in (6) and (7), but boiled two hours after colorless.

The results obtained are shown in the accompanying table.

These results taken in connection with those previously reported show that it is not safe in the analysis of any class of nitrogenous substances to stop the digestion as soon as the liquid becomes colorless, as is authorized by the methods of the Association of Official Agricultural Chemists.

The association recommends[2] the Arnold-Wedemeyer modification of the Gunning method for the determination of nitrogen in peppers in order to insure complete ammonification of the alkaloid nitrogen present. The Arnold-Wedemeyer process differs from that of Dyer simply in that the former uses mercury, copper and potassium sulphate in the digestion, while the latter omits the use of copper, thus reducing the number of reagents and securing a colorless solution. In order to find whether the use of copper gives a higher result, the two processes were compared on black and white pepper, tobacco and two of the cinchona alkaloids with the following results:

	Percentage of nitrogen found.	
Sample	Dyer process (using no copper). Digestion continued 2 hours after colorless or 2½ to 3 hours in all.	Arnold-Wedemeyer process (using copper). Digestion continued 3 hours.
Black pepper.....	2.32	2.31
White pepper	1.83	1.87
Tobacco	3.14	3.14
Cinchonine sulphate	7.65	7.64
Impure quinine.....	8.28	8.22

Taking these results in connection with those obtained by Dyer[3] on atropine, morphine, quinine, strychnine and pyridine, it seems safe to conclude that the use of copper is not necessary either in the case of pepper or of other substances containing nitrogen in the form of alkaloids.

[1] *J. Chem. Soc.*, **67**, 811 (1895).
[2] U. S. Dept. Agr., Bureau of Chemistry. Bull. 65.
[3] *Loc. cit.*

In every case thus far studied the conversion of nitrogen to ammonia had appeared to be complete when the sample was boiled for two hours after colorless, or about three hours in all, with sulphuric acid, mercury and potassium sulphate. Very recently, however, comparative determinations made by one of us (M. J. F.) on some samples of bituminous coal yielded higher results when the solutions, obtained as just described, were further treated with potassium permanganate. The average results for six similar coals were: 1.40 per cent. nitrogen by boiling with sulphuric acid, mercury and potassium sulphate for three hours; 1.59 per cent. by treating in the same manner and then adding permanganate. One or two of the samples were treated by the Arnold-Wedemeyer method. The results were no higher than those obtained by the Dyer method without permanganate.

SUMMARY OF RESULTS.

The experiments here described, taken in connection with other work recently published, lead to the following conclusions:

(1) So many substances yield nitrogen compounds which are colorless in hot sulphuric acid that the disappearance of color from the digesting solution gives little indication of the extent to which ammonification has taken place. When either mercury or potassium sulphate was used alone it was always necessary to digest the solution after it had become colorless in order to secure all of the nitrogen as ammonia. The temperature of the boiling solutions and the total time of boiling are fully as important as the disappearance of color.

(2) Proteids and simple amides, even of aromatic acids, yield their nitrogen as ammonia without especial difficulty. When treated by either the Willfarth or the Gunning method, about 98 to 99 per cent. of the total nitrogen present has usually been converted to ammonia by the time the solution becomes colorless. By continuing the boiling for at least two hours longer or by the careful use of potassium permanganate, most of the remaining nitrogen can be obtained. The complete ammonification of the nitrogen of proteids and amides is more readily and certainly accomplished by the use of both mercury and potassium sulphate, as recommended by Dyer, the boiling being continued for at least one-half hour after the solution becomes colorless, or for at least one hour from the time the potassium sulphate is added.

(3) Aromatic amines also yield colorless solutions before all of the nitrogen has reached the form of ammonia. The amount of nitrogen lost by using mercury or potassium sulphate alone and stopping the digestion as soon as the solution becomes colorless, is greater with naphthylamine than with aniline (acetanilide), and greater with diphenylamine than with naphthylamine. Boiling for two hours longer with either of the reagents alone does not always secure complete ammonification. This is most readily accomplished by using both mercury and potassium sulphate, as in the case of proteids.

(4) Many alkaloids and certain of the so-called "nitrogenous extractives" of plant and animal substances, such as betaine and creatine, yield solutions in sulphuric acid which readily become colorless on boiling after addition of mercury, but less readily yield their nitrogen as ammonium sulphate. In such cases entirely erroneous results are obtained, if ammonification is assumed to be complete when the solution becomes colorless. The use of permanganate to complete the decomposition does not always yield correct results. Potassium sulphate alone sometimes gives much better results than are obtained by the use of mercury alone, probably because the boiling-point of the digesting liquid is higher and a longer time is usually required to obtain a colorless solution. Boiling for one hour with both mercury and potassium sulphate appears to be sufficient for the "nitrogenous extractives," but not for all alkaloids.

(5) Very resistant substances such as alkaloids, coal, etc., should be boiled with sulphuric acid, mercury and potassium sulphate for at least two hours after the solution becomes colorless, and for not less than three hours in all. No advantage has been found in the use of copper in addition to the reagents mentioned, but with the coals tested slightly higher results were obtained by the careful use of permanganate at the end of the three hours' boiling. On account of the danger of loss of nitrogen through too violent a reaction of the permanganate, it is advisable to make the determinations in duplicate, using permanganate in one case and omitting it in the other.

(6) For all samples in which the nitrogen exists essentially as proteids or albuminoids and related compounds, including the called "nitrogenous extractives," and other amides and amino-compounds, it is only necessary to use mercury and potassium sul-

phate, as recommended by Dyer, and to boil for one-half hour after the solution becomes colorless, or in the case of quickly decolorized samples, for at least one hour from the time the potassium sulphate is added.

(7) The Dyer modification appears to combine the advantages of the other methods (Kjeldahl-Willfarth, Gunning and Arnold-Wedemeyer) now recommended by the Association of Official Agricultural Chemists for the determination of nitrogen in organic compounds.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 88].

DERIVATIVES OF COMPLEX INORGANIC ACIDS.

SIXTH PAPER.

BY ALLEN ROGERS AND EDGAR F. SMITH.

Received September 3, 1904.

IN A previous communication[1] from this laboratory, attention was called to complexes of certain sesquioxides with tungstic acid; for example, the aluminico-tungstates and the bismuthico-tungstates, described by Balke and Smith, in which there exist the following ratios between sesquioxide and tungstic acid:

$$1Al_2O_3 : 9WO_3 \text{ and } 2Bi_2O_3 : 11WO_3.$$

The literature on complexes reveals the fact that the sesquioxides which, in the past, have been combined with tungstic and molybdic acids are those of phosphorus, arsenic and antimony, corresponding to the chloride type RCl_3. It might well be expected that bismuth oxide, corresponding to the same chloride type, would enter into combination with tungstic acid in ratios similar to those found among the complex phosphorico-, arsenico- and antimonico-tungstates and molybdates. This surmise proved correct, for among the many derivatives of complex acids containing those oxides, synthesized by Wolcott Gibbs, appear the analogues of phosphorus, more particularly the compound

$$2Na_2O.4P_2O_5.22WO_3.37H_2O$$

with which

$$6(NH_4)_2O.4Bi_2O_5.22WO_3.20H_2O$$

[1] This Journal, **25**, 1229.

and other salts are, without question, analogous. The harmony becomes evident upon doubling the formulas first given them by Balke and Smith.

Aluminium oxide conforms not only to the RCl_3-type of chlorides, but also to the R_2Cl_6-type. The ratio found in the aluminico-tungstates was

$$1Al_2O_3 : 9WO_3.$$

By doubling this proportion so that it reads

$$2Al_2O_3 : 18WO_3,$$

complete analogy with existing tungstates is established. Thus,

$$6(NH_4)_2O.2Al_2O_3.18WO_3.36H_2O$$

would accord well with

$$7(NH_4)_2O.2As_2O_3.18WO_3.18H_2O$$

prepared by Wolcott Gibbs.

Would other sesquioxides—those generally regarded as certain analogues of the chloride type R_2Cl_6—exhibit new ratios between the sesquioxide and tungstic acid, or would they, too, incline to the ratio manifested by oxides like P_2O_3, As_2O_3 and Sb_2O_3? To answer this question, experiments were instituted with the view of combining the oxides of manganese and nickel (R_2O_3) with tungstic acid. Accordingly, Howard W. Brubaker[1] boiled 15 grams of ammonium paratungstate in a liter of water with an excess of manganic hydroxide[2] for twelve hours. The hot solution, pink in color, was filtered and reduced to a small volume upon a water-bath. After standing in a cool place for several hours large, red-colored, octahedral crystals separated. They were recrystallized and proved to be very readily soluble in water. Their analysis gave

	Per cent.
$(NH_4)_2O$	5.77
Mn_2O_3	4.48
WO_3	78.24
H_2O	11.51

from which was deduced the formula

$$4(NH_4)_2O.Mn_2O_3.12WO_3.23H_2O.$$

[1] See Thesis, 1904.

[2] Made by passing chlorine gas through manganous carbonate suspended in water at the room temperature.

Here the ratio of sesquioxide to tungstic acid is in perfect accord with the ratios observed in the aluminico-, ferrico-, and chromico-molybdates of Struve,[1] and by doubling the above formula so that it would read

$$8(NH_4)_2O.2Mn_2O_3.24WO_3.46H_2O$$

its analogue is found in Wolcott Gibbs'

$$4(NH_4)_2O.2P_2O_3.24MoO_3.31H_2O.$$

That is, in this manganico-tungstate there is reason to believe that the manganic oxide betrays a kinship to acid oxides, like those of phosphorus, arsenic and antimony

In making the nickel derivatives the hydrated sesquioxide of nickel was boiled in an ammoniacal solution of ammonium paratungstate for eight hours. The filtered solution was blue in color. It acquired a green tint upon concentration when the ammonia was driven out. There was also a simultaneous separation of a green powder which, however, redissolved on the addition of ammonium hydroxide, the blue color being at the same time restored to the liquid. By keeping it ammoniacal during the evaporation, there separated at last a greenish white crystalline powder. This compound was prepared repeatedly and showed the same characteristics. After freeing it from any contaminating ammonium paratungstate it was analyzed, giving results corresponding to the formula

$$3(NH_4)_2O.Ni_2O_3.16WO_3.22H_2O.$$

	Found.				Theory.
	I.	II.	III.	IV.	
$(NH_4)_2O$	3.59	3.53	3.52	3.53	3.52
Ni_2O_3	3.97	3.93	3.68	4.06	3.73
WO_3	82.90	82.94	83.58	82.88	83.80
H_2O	8.95	9.54	9.60	9.53	8.95

This salt was very sparingly soluble in water after it had once separated from its solution so that to obtain other derivatives, *c. g.*, the barium salt, barium chloride was added to the liquid remaining after filtering out the ammonium salt. In this way a white, very insoluble precipitate was procured which, after washing, was dried and analyzed, giving results corresponding to the formula

$$19BaO.Ni_2O_3.16WO_3.$$

[1] *Am. Chem. J.*, 7, 417.

	Found.			
	I.	II.	III.	Theory.
BaO	43.29	42.95	43.12	42.91
Ni_2O_3	2.53	2.86	2.69	2.44
WO_3	54.18	54.19	54.19	54.65

It may be worth while to observe here that another ammonium salt was obtaind by conducting ammonia through the solution of ammonium nickelico-tungstate during evaporation. The second salt was dark blue in color when moist, but on drying became light blue. Its analysis gave results approximating those required by the formula

$$(NH_4)_2O.Ni_2O_3.4WO_3.7H_2O.$$

	Found.		
	I.	II.	Theory.
$(NH_4)_2O$	4.27	4.27	4.09
Ni_2O_3	13.82	13.95	13.09
WO_3	71.75	71.93	72.99
H_2O	10.16	9.85	9.92

It is needless to add that the perfect removal of nickel from tungstic acid is difficult to accomplish.

Two ratios, then, are present in the nickelico-tungstates:

$$1Ni_2O_3 : 16WO_3 \text{ and } 1Ni_2O_3 : 4WO_3.$$

If the formula of the second salt be doubled, it becomes

$$2(NH_4)_2O.2Ni_2O_3.8WO_3.14H_2O,$$

which has its analogue in

$$3BaO.2As_2O_3.8MoO_3,$$

prepared by Wolcott Gibbs. In other words, in this derivative the nickel oxide is in harmony with the oxides of phosphorus, arsenic and antimony. In the salts

$$3(NH_4)_2O.Ni_2O_3.16WO_3.22H_2O$$

and

$$19BaO.Ni_2O_3.16WO_3$$

there exists a ratio not previously noticed among the complex tungstates, but present in several of Struve's molybdates:

$$5K_2O.Mn_2O_3.16MoO_3.21H_2O,$$

$$5(NH_4)_2O.Mn_2O_3.16MoO_3.12H_2O.$$

It would appear, therefore, taking into consideration also molybdates, that the sesquioxides of manganese and nickel not only imitate P_2O_3, As_2O_3 and Sb_2O_3 in their ratio combinations with tungstic and molybdic acids, but that they show another ratio

$$1Ni_2O_3 : 16WO_3 \text{ and } 1Mn_2O_3 : 16MoO_3,$$

in which they perhaps follow the other type of chloride, assumed by many sesquioxides.

In one of the admirable contributions[1] of Wolcott Gibbs upon complexes, that investigator remarks: "It still remains to study the relations of the oxides of the cerium and yttrium groups to molybdic and tungstic oxides, since these correspond to chlorides of the type RCl_3, and yet differ in a very marked degree from oxides like As_2O_3, Sb_2O_3, etc., etc."

The following paragraphs contain the results reached by combining such oxides with tungstic acid. The new compounds were prepared in practically the same way so that a general description will apply to all. Ammonium paratungstate in aqueous solution was boiled with the respective hydroxides in excess for eight hours (as in the case of nickel). After filtration the solution was evaporated to dryness on a water-bath. In every case a salt separated as the concentration proceeded. This was examined and found to vary in composition, due, no doubt, to its instability. If it was not removed, it dissolved, becoming later an oil, which finally dried down to a transparent gum.

All of the salts to be described proved quite insoluble after they had become dry, so that very little could be learned regarding their chemical behavior.

Ammonium Prasedymico-tungstate,

$$2(NH_4)_2O.Pr_2O_3.16WO_3.16H_2O.$$

—This salt was obtained in the form of a green transparent gum. It was very sparingly soluble in water. Alkalies and acids quickly decomposed it. The method of analysis was practically that pursued in former cases with complexes. The ammonia and water were obtained by heating a portion of the salt. The ammonia itself was determined by distillation of the salt with potassium hydroxide and subsequent titration of the acid in which the gas had been collected.

[1] *Am. Chem. J.*, 7, 412.

To estimate the praseodymium a portion of the salt was decomposed by digestion with nitric or hydrochloric acid. After filtering out the tungstic acid the praseodymium was precipitated with ammonia water. The praseodymium hydroxide was again treated with acid, filtering out any tungstic acid which might separate. Even then the praseodymium hydroxide was white in color, totally unlike its usual appearance. This was due to adherent tungstic acid which could only be eliminated by fusing the impure praseodymium oxide with sodium carbonate and potassium nitrate. The tungstic acid was determined by difference.

	Found.			
	I.	II.	III.	Theory.
$(NH_4)_2O$	2.63	2.41	2.39	2.34
Pr_2O_3	7.59	7.56	7.48	7.42
WO_3	83.17	83.47	83.62	83.73
H_2O	6.61	6.56	6.51	6.51

Barium Praseodymico-tungstate,

$$4BaO.Pr_2O_3.16WO_3.7H_2O.$$

—This salt was made by adding barium chloride to the solution poured off from the ammonium salt. It was a white precipitate, insoluble in water. It was washed by decantation, dried and analyzed.

	Found.		
	I.	II.	Theory.
BaO	12.96	12.41	12.80
Pr_2O_3	6.84	....	6.88
WO_3	77.51	78.68	77.67
H_2O	2.69	....	2.65

Attempts to prepare it a second time failed, but no trouble was experienced in making the following compound:

$$6BaO.Pr_2O_3.16WO_3.9H_2O,$$

the analyses of which agree very well and give it definiteness.

	Found.			
	I.	II.	III.	Theory.
BaO	17.54	17.36	17.45	17.92
Pr_2O_3	6.61	6.52	6.45	6.42
WO_3	72.70	72.97	73.35	72.48
H_2O	3.15	3.15	3.15	3.18

Silver Praseodymico-tungstate,

$$4Ag_2O.Pr_2O_3.16WO_3.8H_2O.$$

—This was prepared like the barium salt. Its color was greenish white. It was insoluble in water. Its analysis proved troublesome.

	Found.	Theory.
Ag_2O	18.43	18.15
Pr_2O_3	6.38	6.43
WO_3	72.48	72.59
H_2O	2.71	2.83

Ammonium Neodymico-tungstate,

$$3(NH_4)_2O.Nd_2O_3.16WO_3.20H_2O.$$

—This salt is pink in color. It dissolved in water with great difficulty. Its analysis proved difficult. The removal of the last traces of tungstic acid could only be effected by fusing the neodymium oxide with a mixture of sodium carbonate and potassium nitrate. The neodymium was weighed as Nd_4O_7.

	Found.			
	I.	II.	III.	Theory.
$(NH_4)_2O$	2.80	2.92	2.86	3.42
Nd_2O_3	6.82	7.22	7.02	7.34
WO_3	82.78	82.24	82.51	81.35
H_2O	7.60	7.62	7.61	7.89

Barium Neodymico-tungstate,

$$6BaO.Nd_2O_3.16WO_3.17H_2O.$$

—This salt was also pink in color and quite insoluble in water. Its analysis showed:

	Found.		
	I.	II.	Theory.
BaO	17.16	17.18	17.44
Nd_2O_3	6.40	6.74	6.33
WO_3	69.43	69.22	70.39
H_2O	7.01	7.09	5.84

The discrepancies here are due to the extreme difficulty in obtaining the salt pure because of its insolubility, and also to troubles which arose in the analysis, simple though it would seem.

Ammonium Lanthanico-tungstate,

$$2(NH_4)_2O.La_2O_3.16WO_3.16H_2O.$$

—This salt was prepared like its analogues. It was white in color and showed the same great insolubility as the other complexes of this group.

	Found.			
	I.	II.	III.	Theory.
$(NH_4)_2O$	2.59	2.59	2.59	2.35
La_2O_3	7.06	6.49	7.06	7.29
WO_3	84.56	84.68	84.11	83.87
H_2O	6.29	6.24	6.24	6.49

Barium Lanthanico-tungstate,

$$5BaO.La_2O_3.16WO_3.16H_2O.$$

—A white salt, made by precipitation of the extremely dilute solution of the preceding salt with barium chloride.

	Found.			
	I.	II.	III.	Theory.
BaO	....	15.84	....	15.03
La_2O_3	6.52	6.21	6.92	6.34
WO_3	....	72.63	73.67	72.97
H_2O	5.42	5.32	6.08	5.66

Silver Lanthanico-tungstate,

$$5Ag_2O.La_2O_3.16WO_3.4H_2O.$$

—This salt was made like the preceding barium salt. It was white in color and very insoluble.

	Found.				
	I.	II.	III.	IV.	Theory.
Ag_2O	....	22.43	....	22.28	22.04
La_2O_3	6.57	6.70	6.63	6.27	6.13
WO_3	....	69.38	....	70.18	70.47
H_2O	1.49	1.49	1.49	1.49	1.36

Ammonium Cerico-tungstate,

$$2(NH_4)_2O.Ce_2O_3.16WO_3.2H_2O.$$

—The solution of ceric hydroxide in ammonium paratungstate was at first colorless, but upon concentration it became yellow and finally red. From this, on standing, was obtained a red transparent glass, which, once dry, would not dissolve in water and on boiling with it sustained decomposition.

	Found.				
	I.	II.	III.	IV.	Theory.
$(NH_4)_2O$.....	2.70	2.56	2.59	2.63	2.31
Ce_2O_3.....	7.55	7.19	7.23	6.97	7.28
WO_3.....	81.96	82.56	82.51	82.78	82.41
H_2O	7.79	7.69	7.67	7.62	8.00

Wolcott Gibbs,[1] in his last published paper on the derivatives of complex inorganic acids, mentions briefly a molybdate in which cerium oxide was present. No analyses are given.

As frequently observed in the earlier sections of this communication the products therein described were extremely insoluble. It proved to be one of the obstacles in the path of eliminating all possible contaminating bodies. When, however, a pentoxide was introduced into any one of these compounds the resulting, new derivative proved to be exceedingly readily soluble in water. This was especially true of the ammonium salts of lanthanico-vanado-tungstic acid and praseodymico-phospho-tungstic acid.

Klein studied four series of borico-tungstates. In one series he found the ratio

$$2R_2O.B_2O_3.9WO_3.$$

Here again is the ratio 1 : 9, the same ratio which Balke and Smith found in the aluminico-tungstates; but, as noted in the earlier portion of this paper, by doubling the formula so that it became

$$2Al_2O_3 : 18WO_3$$

harmony with an existing arsenico-tungstate was found; hence, there would now be

$4R_2O.2B_2O_3.18WO_3$	Klein,
$6R_2O.2Al_2O_3.18WO_3$	Balke and Smith,
$7R_2O.2As_2O_3.18WO_3$	Gibbs.

Attention, too, was called in previous paragraphs to the analogy evident in the nickelico-tungstates and the arsenico-molybdates, as well as to that between the bismuthico- and phosphorico-tungstates, also the manganico-tungstates and the phosphorico-molybdates, which would arrange in a series the oxides

B_2O_3, Al_2O_3, P_2O_3, Mn_2O_3, Ni_2O_3, As_2O_3, Sb_2O_3, and Bi_2O_3,

[1] *Am. Chem. J.*, **17**, 1895.

harmonizing with the chloride type RCl_3, and yet there is proof in the compound—

$$3(NH_4)_2O.Ni_2O_3.16WO_3—$$

and in the molybdate—

$$5(NH_4)_2O.Mn_2O_3.16MoO_3—$$

that the sesquioxides—Ni_2O_3 and Mn_2O_3—point to a possible ratio between oxides of that constitution and tungstic and molybdic acids, which had not previously been observed except in the case of Struve's manganico-molybdate, but which ratio, from the results obtained in the study of the complexes resulting from the union of the rare earth oxides with tungstic acid, is evidently a definite and important ratio, *viz.*:

$$1R_2O_3 : 16WO_3;$$

otherwise it would scarcely be expected to appear so well marked in such a series of derivatives as that presented above.

If it were permissible to arrange the oxides which have been combined with tungstic and molybdic acids in groups, they would appear thus:

I.		II.	III.
B_2O_3			
Al_2O_3			
P_2O_3	2 : 24	Mn_2O_3 }	1 : 16 { Nd_2O_3
As_2O_3	2 : 8	Ni_2O_3 }	Pr_2O_3
Sb_2O_3			La_2O_3
Bi_2O_3			Ce_2O_3

Under I would occur the oxides which are credited with decided acid character. The ratios they exhibit in their combinations with tungstic and molybdic acids are more numerous than has been noticed with the oxides under II and III. Those under II—manganic and nickelic oxides—may be viewed as transitional oxides. In Wolcott Gibbs' interpretation of Struve's salts,[1] ferrico-, aluminico- and chromico-molybdates exist in which the ratio of the oxides Al_2O_3, Cr_2O_3 and Fe_2O_3 to molybdic acid is as 1 : 12. There is no evidence of other ratios. This one ratio, however, would be sufficient, as in the case of Mn_2O_3, to ally them with P_2O_3, As_2O_3 and Sb_2O_3. Whether other ratios will show themselves in their combinations with tungstic acid remains to be

[1] *Am. Chem. J.*, **7**, 417.

seen. In one instance an aluminico-tungstate (1 : 12 or 2 : 24) was noticed together with the usual 2 : 18-compound. Its quantity was never very great.

The ferrico-, chromico- and cobaltico-tungstates are being investigated.

In conclusion, the writers would here acknowledge their indebtedness and extend thanks to Dr. H. S. Miner, of the Welsbach Lighting Co., for the generous gift of rare earth salts, and to Messrs. Dox, Masland and Poole, for valuable and patient assistance in the analytical work connected with this study.

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AN INVESTIGATION OF SODAMIDE AND OF CERTAIN OF ITS REACTION-PRODUCTS.[1]

BY W. PHILLIPS WINTER.

Received June 10, 1904.

THE history of the preparation of sodamide dates from 1809, when Sir Humphry Davy,[2] in England, and Gay-Lussac and Thénard,[3] in France, almost simultaneously discovered the amides of sodium and of potassium. They were carrying on investigations to determine the composition of ammonia and they led a strong current of the latter gas, for several hours, over the pure metal heated in a glass retort to about 300°. The glass of the retort was considerably etched, and the semicrystalline mass of sodamide obtained was olive-green in color.

They investigated and sought to analyze it. Davy plunged pieces of sodamide under the mouths of jars filled with water, transferred the unabsorbed gas to a eudiometer and determined that hydrogen was formed in the decomposition of sodamide by water. Gay-Lussac and Thénard, by strongly heating the substance, obtained two-fifths of the ammonia that had disappeared in the reaction; at a higher temperature nitrogen and hydrogen gases were formed in the ratio of 2.5 of the former to 1 of the latter in quantities to account for one-fifth more of the ammonia. Decomposition of the residue by water yielded the remaining portions of ammonia.

[1] The work herein described is abstracted from a dissertation for the degree of Doctor of Philosophy in the Johns Hopkins University. It was carried on under the guidance of Professor E. Renouf.

[2] *Phil. Trans.*, **1**, 39 (1809).

[3] *Recherches Physico-chimiques*, **1**, 337-356.

These investigators are also responsible for a method, published by them, for the preparation of sodium nitride. They stated that when sodamide is strongly heated it decomposes in accordance with the equation

$$3NaNH_2 = Na_3N + 2NH_3.$$

They described the nitride as a dark brown powder. Titherly,[1] in 1894, carefully repeated these experiments, employing a pure quality of sodamide, and he found that strong heat completely dissociates it. He concluded that the so-called nitride was to be ascribed to impurities in the sodium employed and to contamination by the constituents of the glass of the retorts.

Beilstein and Geuther,[2] in 1858, prepared sodamide in the same way as the discoverers did. They analyzed it by determining the amounts of sodium and of ammonium chlorides formed when it was decomposed by hydrochloric acid, and they further investigated its reaction products when currents of dry carbon monoxide, carbon dioxide and carbon disulphide were led over the heated sodamide. The reactions are,

$$NaNH_2 + CO = NaCN + H_2O,$$
$$2NaNH_2 + CO_2 = CNNNa_2 + 2H_2O,$$
$$NaNH_2 + CS_2 = NaCNS + H_2S.$$

The presence of water produced secondary reactions with sodamide not included in the equations.

Drechsel[3] showed that the reaction with carbon dioxide was not analogous with the one given for carbon disulphide and he proved that the nature of the reaction with carbon dioxide was better expressed in consecutive stages, thus:

(*a*) $CO_2 + NaNH_2 = OC\begin{<}NH_2\\ONa\end{>}$, sodium carbamate;

(*b*) $NH_2COONa + \text{heat} = H_2O + NCONa$, sodium cyanate;

(*c*) $NCONa + NaNH_2 = H_2O + CNNNa_2$, disodium cyanamide;

the reaction evidently proceeding one step farther than in the case of carbon disulphide.

[1] *J. Chem. Soc.* (London), **65**, 504, and **71**, 460.
[2] *Ann. Chem.* (Liebig), **108**, 88.
[3] *J. prakt. Chem.* (2), **11**, 308; and **16**, 203.

Wislicenus[1] heated sodamide in a stream of dry nitrous oxide. It affords a simple and effective means for the synthesis of sodium triazoate,

$$NaNH_2 + N_2O = NaN_3 + H_2O.$$

This method has been recently considerably improved by Dennis and Browne.[2]

Titherly[3] carried on an extensive investigation of sodamide. He made the discovery that it can be made in vessels of pure metal, such as silver or iron, in considerable quantity and free from the contaminations that glass always imparts to it. Sodamide thus made is of a pure white color. Titherly employed two different synthetical methods for the analysis of his product, the results of which confirmed each other and pointed conclusively to the hitherto accepted formula for sodamide. He further showed that disodimide and sodium nitride could not be formed by continued substitution of ammonia hydrogen by sodium, but that certain organic residues have the power to substitute one or both of the hydrogen atoms of sodamide.

The preparation of sodamide presents no especial difficulties. Fig. 1 represents the apparatus as used. *A* is a flask in which concentrated ammonia water is heated with a low flame. *B* is an empty gas-washing bottle, kept cool to condense excess of moisture. 1, 2, 3 and 4 are drying towers, filled with soda-lime. *C* is a tube filled with pieces of sodium. It may conveniently be about 40 cm. long. *D* is a wrought iron retort, made in two parts, which fit together at the flange in the center. It is capable of holding about 200 grams of sodium when filled nearly to the flange. Before heating the sodium, ammonia is passed for a long time through the apparatus, and at the conclusion of the experiment the sodamide is allowed to cool in the current of ammonia. Precautions are taken to have a *continuous* supply of ammonia.

The writer has found, by careful tests, that a silver-plated crucible is rapidly attacked, but that a pure wrought iron crucible can be used repeatedly, the sodamide formed in it showing no trace of iron when its solution in water was acidified and treated with potassium ferrocyanide. The crucible was heated for about

[1] *Ber. d. chem. Ges.*, **25**, 2084.
[2] This Journal, **26**, 577.
[3] *Loc. cit.*

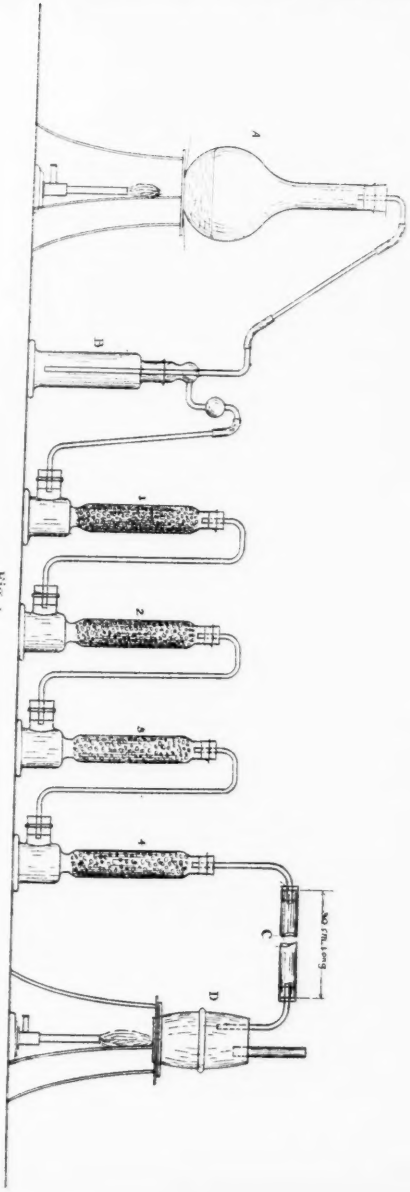

Fig. 1.

five hours with a single Bunsen burner, so regulated as to prevent the distillation of the sodamide into the air. More elaborate apparatus has been described for the preparation of sodamide, but the chief merit of the apparatus here described is that it can be quickly put together from apparatus to be found in almost any laboratory and with it sodamide of excellent quality has been repeatedly made.

Omitting the discussion of the better known properties of sodamide, we have noted that under certain circumstances, not fully understood as yet, sodamide kept in dry, glass-stoppered bottles slowly undergoes a peculiar color change from white to yellowish brown. The change is more rapid if the sodamide is powdered. Light or its absence was not responsible for the change. It does not necessarily depend on the method of its manufacture for samples of the same sodamide were powdered and kept side by side in different vessels for some weeks. The change had taken place in part of the samples only. The change is, in some way, dependent on the amount of dry air which comes in contact with the sodamide and upon the duration of exposure to it, for it was observed that: (1) The sodamide which had been kept longest had undergone the greatest change when conditions otherwise were the same; (2) small bottles, with *accurately fitting* stoppers, not opened repeatedly, as many of the samples were, underwent little or no change in their contents; (3) the powdering of sodamide brings the air more completely into contact with the sodamide.

When sodamide is thrown into water the behavior is quite similar to that of sodium, forming a globule which floats about on the water and at last explodes. The globule formed by sodamide that has undergone the color change often changes to a brown or black color and explodes with increased violence. If the water is warm, these phenomena are more noticeable. It was the peculiar sharp explosion that first suggested the possibility of the presence of traces of a triazoate or some such compound as a working hypothesis.

Sodamide is rapidly decomposed by absolute alcohol with evolution of ammonia and formation of sodium ethylate. The alcohol is heated to boiling, if the sodamide is added rapidly, but since it does not float on the alcohol there is no final explosion. While the white sodamide imparts no color to the alcohol until after long

standing, the yellow variety colors it a deep brown, out of all proportion to the color in the sodamide used. With the yellow variety there is usually formed also an insoluble residue.

Examination of the Insoluble Gases Formed on Decomposing Sodamide with Water.—It has long been known that water breaks down sodamide into sodium hydroxide, setting free ammonia; and Davy also noted the formation of hydrogen. In all the sodamide examined by the writer there was found also traces of nitrogen, the ratio between hydrogen and nitrogen depending not only on the way in which the sodamide was prepared, but also on

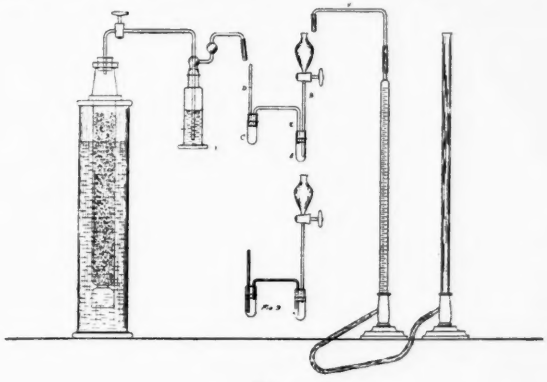

Fig. 2.

the length of time and manner in which it was kept previous to analysis. The apparatus in which these experiments were carried on is represented in Figs. 2 and 3. Carbon dioxide, dried by sulphuric acid, was first conducted through the apparatus (Fig. 2), the gas entering at *D* and escaping at *B*. The weighed substance (finely powdered) was then introduced into *A* and the current of carbon dioxide continued until the gas, issuing from *B*, was *completely* absorbed by a strong solution of caustic soda. Without removal of the stoppers the tubes were shifted into the position shown in Fig. 3, the stop-cock of *B* closed and the funnel filled with distilled water. The tube *D* was connected to the capillary of a Hempel's burette, *F*, completely filled with a 10 per cent. solution of caustic soda. In some experiments it was found necessary to introduce into the burette measured portions of pure oxygen. Water was slowly dropped from the funnel into the

sodamide, diminished pressure being produced in the burette. At the end, water was admitted to drive over every trace of gas, and the carbon dioxide and ammonia were completely absorbed.

Hydrogen was determined by explosion in a eudiometer, the nitrogen being estimated by difference. The identity of nitrogen was established beyond question by sparking known volumes of it in the presence of excess of oxygen and traces of caustic potash for several hours with a high voltage current. The gas remaining was then completely absorbed by phosphorus.

In the experiments there was employed: (1) Sodamide which had been insufficiently heated, all visible excess of sodium having been mechanically removed: (2) sodamide which had been properly made; (3) sodamide which had been kept until it had undergone the color change referred to.

From a large number of results, which are quite concordant, the following summary is drawn: (1) The relative proportion of nitrogen to hydrogen is low in sodamide that has been insufficiently heated, but high in sodamide properly prepared; (2) the ratio of nitrogen to the total insoluble gases formed increases both relatively to the hydrogen and absolutely after sodamide has been kept for some time; (3) free nitrogen is always given off in small amounts when sodamide is decomposed by water.

Approximately 0.6 gram of freshly prepared sodamide, insufficiently heated, yielded 17 cc. of insoluble gases, of which 16 per cent. was nitrogen. Six weeks later 0.4 gram of the same sample yielded 13.7 cc. of gases, of which 65.8 per cent. was nitrogen. 0.85 gram of sodamide, properly prepared, yielded 5 cc. of gases of which 72.5 per cent. was nitrogen; 14 weeks later 0.92 gram of the same sample yielded 6.65 cc. of gases, of which 92 per cent. was nitrogen. Since the amount of gas obtained from a sample of sodamide that has been heated a sufficiently long time is so much less and the ratio of nitrogen so much higher, we can not escape the conclusion that the hydrogen is due to minute particles of sodium, invisible to the unaided eye, and that these are gradually converted into sodamide at the *ordinary* temperature by the atmosphere of ammonia always present over sodamide. The source of nitrogen has not been satisfactorily explained as yet, and it is still under investigation. A provisional theory, which has every indication of probability, will be referred to in connection with the next phase of the investigation.

If the water solution of the yellow sodamide is acidified, nitric oxide is given off; none is obtained when freshly made sodamide is similarly treated. The water solution of yellow sodamide was placed in an apparatus similar to the one described under Fig. 2, and the air was displaced in the same way. Sulphuric acid was admitted from the funnel and the gases evolved were collected in a Hempel burette. The amount of nitric oxide present after absorption of the carbon dioxide was determined both by absorption in ferrous sulphate solution and by admitting measured portions of oxygen and noting carefully the diminution in volume. The mean of several experiments indicated that somewhat more than half of the gas thus obtained was nitric oxide, while the remainder was nitrogen. We thus have nitrogen occurring as a product when sodamide is decomposed by water, and again when the water solution of yellow sodamide is treated with acids. The nitrogen source cannot be the same in both cases. Qualitative tests of the water solution for nitrous and hyponitrous acids were made, a considerable amount of the former, but only traces of the latter, being indicated.

To account for the presence in sodamide of these bodies capable of yielding nitrogen and its oxides, recourse must be had to the well-known slow oxidation which ammonia can undergo; thus,

$$2NH_3 + 4O \rightarrowtail 2NH(OH)_2 \rightarrowtail HON : NOH + 2H_2O.$$

The first product is unknown, the second is hyponitrous acid. If oxidation stops at this stage, the unstable hyponitrous acid breaks down into nitrous oxide and water, and the formation of nascent nitrous oxide lends some probability to the suggested explanation that a compound is formed by it with sodamide analogous to, if not identical with, sodium triazoate. It can not be denied that a reaction which proceeds rapidly at a definite elevated temperature may also proceed with greatly reduced velocity at ordinary temperatures. Since the decomposition of sodamide by water in the apparatus described above, takes place with extreme violence and with sudden rise of temperature, the presence of traces of such triazoate will readily account for the small amount of nitrogen obtained from freshly prepared sodamide and for larger amounts in that which has stood for some time in contact with dry air.

But continued action of oxygen upon ammonia yields nitrous and finally nitric acids, and the undoubted presence of nitrous

acid in appreciable quantity, along with traces of hyponitrous acid, serves to confirm the theory. The decomposition of nitrous acid by mineral acids readily accounts for the nitric oxide, but not for the nitrogen.

Hyponitrous acid may break down in either of two ways, yielding, according to the one, which is the more common method, nitrous oxide and water; but when suddenly or violently decomposed the products are water, nitrogen and oxygen. The oxygen would be removed by the excess of nitric oxide, thus accounting for the brown fumes always noted for a short time in the apparatus, despite the utmost care to exclude all traces of air.

Sodium Cyanamide from Sodamide.—Beilstein and Geuther[1] have already shown that when dry carbon dioxide is passed in a slow stream over heated sodamide sodium cyanamide, $CNNa_2$, is formed. In the course of certain experiments by the writer it was noted that when a cylinder containing a small amount of water, heated almost to boiling, was connected to the carbon dioxide generator, so that there might be a continued supply of the gas, a shower of brilliant sparks occurred when sodamide, finely powdered, was sifted into the cylinder. The reaction was most complete when the temperature of the water was between 60° and 100°, and when the gas in the cylinder was not too much diluted with hydrogen, nitrogen or air.

Examination of the water solution at the end of the experiment showed the presence of cyanamide, the most satisfactory yield being found in those experiments in which there had been the greatest production of sparks. A quantitative analysis was made of the silver cyanamide produced by addition of ammoniacal silver nitrate solution to a solution of cyanamide or any of its salts. After drying the amorphous, brilliant yellow silver cyanamide at 130° for a sufficient time, the analysis was carried on as follows:

(1) For silver, gravimetrically as silver chloride. 0.3576 gram gave 0.3930 gram AgCl, equivalent to 0.2958 gram Ag, or 82.71 per cent. The theory calls for 84.34 per cent.

Beilstein and Geuther obtained { 81.34 per cent. / 81.68 per cent.

Drechsel obtained { 80.6 per cent. / 81.6 per cent.

Mulder obtained 82.9 per cent.

[1] *Loc. cit.*

It was pointed out by Mulder that the explanation for these uniformly low results was probably to be found in the presence of silver dicyandiamide, $C_2N_4H_3Ag$, in small quantity, formed through the tendency to polymerize, so frequently displayed by cyanogen compounds.

(2) For nitrogen, volumetrically by Dumas' method, giving 11.37 per cent.; calculated, 10.97 per cent.

(3) For carbon and hydrogen by combustion with copper oxide in presence of a copper spiral, which gave, C, 5.47; H, 0.35; calculated, C, 4.68 per cent.

These results for nitrogen and carbon serve to confirm the presence of a polymer of cyanamide for, while a portion of the water obtained may not unlikely be attributed to traces of moisture absorbed by the apparatus and reagents or imperfectly removed from the oxygen, it is hardly probable that both nitrogen and carbon should be in excess of the theoretical, while at the same time silver was deficient, unless traces of a compound were present containing a higher proportion of carbon and of nitrogen and a lower one of silver, as silver dicyandiamide does.

SODAMIDE AND PHOSPHORUS PENTACHLORIDE.

A number of weeks after the investigation, herein described, had been commenced, Stock and Hoffman[1] published an account of the preparation of a new nitride of phosphorus, P_3N_5, by treating phosphorus pentasulphide with liquid ammonia and heating the complex compound formed. It may also be formed by heating the pentasulphide directly in a stream of ammonia gas to 230°.

It seemed not improbable that sodamide, acting on phosphorus pentachloride, could effect a transformation such as

$$3PCl_5 + 10NaNH_2 = P_3N_5 + 5NH_4Cl + 10NaCl,$$

or

$$3PCl_5 + 15NaNH_2 = 3(P(NH_2)_5) + 15NaCl,$$
$$3(P(NH_2)_5) + \text{heat} = P_3N_5 + 10NH_3,$$

or some similar compound of phosphorus with amidogen or its residue.

The work of Joannis,[2] who obtained boron triamide by passing the vapor of boron trichloride together with hydrogen through liquid ammonia; of Hugot,[3] who worked with sodammonium,

[1] *Ber. d. chem. Ges.*, **36**, 314.
[2] *Compt. Rend.*, **135**, 1106.
[3] *Ibid.*, **121**, 206; **126**, 1719; **127**, 553.

$NaNH_2$, on phosphorus and on arsenic; of Besson,[1] who obtained as a final product phospham, PN_2H, from the double salt obtained by treating phosphorus pentachloride with ammonia; and of others who have used liquid ammonia and ammonia gas, points clearly to the fact that compounds containing ammonia-nitrogen have been made in considerable variety and are of unusual chemical interest.

Preparation.—When powdered sodamide and phosphorus pentachloride are brought together in *small quantities* in a dry test-tube and the mixture slightly warmed a violent reaction ensues, accompanied by flame and by the evolution of a white extremely light powder, the greater part of which settles on the sides of the tube. The bottom of the tube is usually melted out by the heat generated. The white powder, which had sublimed on the walls of the tube, was collected and thrown into water. The greater part of it dissolved readily, and this was found by qualitative tests to consist of ammonium chloride, sodium chloride, and traces of phosphorus compounds. A small portion was found to be insoluble in water.

The results attained in this rough qualitative way seemed to warrant more careful experiment, and accordingly the following apparatus was devised for the work: A large bell-jar of about 20 cm. diameter and 30 cm. in height was fitted to a ground glass plate from which had been cut a portion of sufficient width to admit the glass tube through which pure nitrogen was admitted. The nitrogen, made from molecular equivalent amounts of sodium nitrite and ammonium chloride, was stored in a gasometer, washed through three drying bottles containing strong sulphuric acid and passed over heated copper gauze to remove traces of oxygen and of oxides of nitrogen. Fitted tightly into the neck of the bell-jar was a wide glass tube, which could be raised or lowered at will. To the top of the tube was attached a funnel which served to direct the fall of the materials to be introduced into the small porcelain dish placed within the jar. A slow stream of nitrogen was conducted into the apparatus for a considerable time, the tube in the neck of the bell-jar having been drawn up its full length to facilitate the expulsion of air from the apparatus. Without interrupting the flow of gas, small, nearly equal, portions of powdered sodamide and of phosphorus pentachloride were

[1] *Compt. Rend.*, **114**, 1264.

alternately dropped through the funnel tube, which had been partially lowered. The reaction usually took place at once, but if not, a warmed glass rod, inserted through the tube, was sufficient to start the reaction. The energy of the reaction in the atmosphere of nitrogen is much less than in the air, and if care is exercised in the successive addition of the two reacting materials, very little of the white product was projected into the air. Sufficient heat was generated by the union of the first portions to carry the operation on to the end. The time consumed in introducing into the apparatus about 36 grams of phosphorus pentachloride and 30 grams of sodamide was about two hours.

The addition of either reagent in excess soon interrupted ignition of the mixture, but action is at once restored with considerable vigor when change to the other reagent is made. The apparatus was allowed to cool in the stream of nitrogen and upon opening the bell-jar its sides and the bottom plate were found to be covered to a considerable depth with a deposit of a white, light powder in a state of extremely fine subdivision. In the porcelain dish was a solid core consisting largely of sodium chloride and of traces of the reagents used.

Separation and Purification of the Sublimate.—To separate the soluble from the insoluble portions was found to be an exceedingly difficult task. When the powder is thrown into water, much of it goes into solution, a small portion settles, but the water assumes and retains a milky appearance, which does not disappear after two months' standing. It has been found impossible to separate and purify the residue in this way. The pores of the paper or of the asbestos-filter quickly become clogged and the portion of the residue which comes into contact with the filter forms a gummy mass and adheres to it with such tenacity that separation of filter and precipitate is impossible after drying. The yield of insoluble powder is so small that washing by decantation results in almost complete loss of the precipitate. Washing with alcohol or other organic solvents is impracticable, owing to the quite general insolubility of the chlorides which it is desired to remove. If the powder be treated with moderately dilute hot nitric acid, an insoluble residue soon settles and the supernatant liquid becomes clear. Specimens of the powder for analysis were obtained in this way. Brown fumes of nitrogen peroxide were evolved on heating and these were ascribed at first to the action

of the hydrochloric acid formed from traces of phosphorus oxychloride, which are undoubtedly present. The results of analysis indicate that it is far more likely that the oxidation takes place in the insoluble compound itself.

Acetic acid of 25 per cent. strength can also be used to separate the soluble impurities—the powder obtained being somewhat more voluminous. If hydrochloric acid is used, there is also rapid settling of the insoluble residue, but when this is dried at 100° in an air-bath it is semi-liquid and gummy, and on further heating to 145° the mass becomes, after cooling, gray, hard tenacious and vitreous.

The above acids, if diluted further, as well as sulphuric acid or solutions of the fixed alkali hydroxides would not effect separation of the two portions. After decantation from the acid washings the powder was dried in glass vessels at 100° and separated from the glass by the aid of a piece of stiff platinum wire. The yield was about 2.5 per cent. of the weight of sublimate used.

Properties of the Insoluble Portion.—The powder thus obtained was a white, nearly tasteless, odorless compound, exceedingly inert. Boiling with the strong mineral acids did not affect it and similar treatment with aqua regia or with concentrated potassium hydroxide solution affected it, if at all, to so slight an extent as to be unnoticeable, if the action was not prolonged.

Three methods were devised which were effective in decomposing it:

(*a*) Heated with water in a sealed tube for three hours to 180° it was decomposed and the solution, on opening the tube, yielded the odor of ammonia and responded to the molybdate of ammonia test for phosphoric acid.

(*b*) Treated with an aqueous solution of hydrofluoric acid and a little sulphuric acid in a platinum crucible, the compound was broken down upon the application of gentle heat. A solution of the residue gave the test for phosphoric acid.

(*c*) Heated to dull redness for four hours in a combustion tube with a mixture of powdered hydroxide and nitrate of potassium, ammonia was evolved and a phosphate remained behind. A silver boat was used and a slow stream of dry air was forced over the heated mass.

Analysis.—The above methods were all employed in the analysis of the compound. In the practical application of the first

method it was noted that when water alone was used the tube was badly attacked and several grams of silica were separated. It was found best to employ dilute hydrochloric or sulphuric acid for the twofold purpose of diminishing the separation of silica and of fixing the ammonia in the non-volatile condition. In all determinations of phosphoric acid by this method, however, it was necessary to separate silica in the usual way before estimating the phosphorus as magnesium pyrophosphate. The second method was available for the determination of phosphoric acid only. It possessed the advantage of rendering unnecessary the previous removal of silica. The third method was not free from silica contamination, since it was impossible to prevent distillation of the contents of the silver boat on to the combustion tube.

In the first method the ammonium salt was decomposed by distillation with sodium hydroxide, the ammonia being absorbed by a standard acid, while in the third method the ammonia was received directly into the acid.

Powder Purified by Nitric Acid.

Weight. Gram.	Per cent. of P.	Per cent. of N.	Method of decomposition.
0.0864	33.67	19.42	Fusion with KOH and KNO_3 4 hours.
0.0739	40.31	20.58	" " " " " 5 ½ hours.
0.0810	....	21.54	" " " " " 5 ½ hours.
0.0578	40.31	....	By hydrofluoric acid.
0.0638	40.26	20.75	Sealed tube with HCl at 180°.
0.1108	....	21.50	" " " " " 180°.
			Vitreous mass obtained by hydrochloric acid.
0.0630	26.56	15.11	In sealed tube, 180°.
0.1008	27.58	14.57	" " " 180°.

Analysis of portion dissolved out by nitric acid.

Weight of material.	Weight of NH_4.	Weight of Cl.	Weight of P.	Weight of Na.
3.608	0.2879	1.6998	0.2512	0.7382

Corresponding to :

	Grams.
NaCl	1.8735
NH_4Cl	0.8524
H_3PO_4	0.7944
Undetermined	0.0777
	3.608

Interpretation of Results.—Whatever the composition of the compound represented by the above analyses may prove to be,

it is clear that the phosphorus and the nitrogen stand in the ratio of 1 : 1. The results of the analysis of the compound, purified by hydrochloric acid, show that it was, to a considerable extent, broken down and they are, therefore, not considered. The analyses correspond to the formula PO_2N or to some polymer of it. Such a formula requires 40.24 per cent. phosphorus, 41.53 per cent. oxygen, 18.22 per cent. nitrogen. There was found 40.28 per cent. phosphorus, 20.35 per cent. nitrogen. The excess of nitrogen is not surprising when the method of preparation of the material for analysis is considered.

The phosphamic acid described by Schiff,[1] the identity of which was called in question by Gladstone and Holmes,[2] agrees quite well in analysis and in all properties save one, that of its solubility in water, with the compound we have obtained. A series of metaphosphimic acids, PONHOH, empirically isomeric with Schiff's compound has been described by Stokes[3] and he has suggested that in this instance there may possibly occur a complex polymer of metaphosphimic acid, $(PONHOH)_x$. But since nitric acid undoubtedly oxidizes the original product of the reaction and since water probably hydrolyzes it, the analysis, as given, throws little light on the original product of the energetic reaction between phosphorus pentachloride and sodamide.

SODAMIDE AND YELLOW PHOSPHORUS.

Sodamide and phosphorus exhibit an energetic reaction when brought together in a test-tube and slightly warmed. In an endeavor to control this reaction the above reagents were heated together in benzene, xylene, aniline, and paraffin oil successively to the respective boiling-points of these liquids, but there was no direct combination between the sodamide and phosphorus. But when the reaction occurs in glass vessels of any kind the glass is invariably broken by the sudden heating, thus preventing the preparation of any considerable amount of the material. The products of the reaction were found to consist of some red phosphorus and of particles of a black compound which, when thrown into water, produced inflammable phosphine. Red phosphorus and sodamide heated together rather more strongly produced a similar compound.

[1] *Ann. Chem.* (Liebig), **103**, 168.
[2] *J. Chem. Soc.* (London), **17**, 226.
[3] *Am. Chem. J.*, **15**, 198, and **18**, 629.

Porcelain vessels could be used without fear of breakage and the experiment whereby about 12 grams could be prepared at one time was carried out as follows: The bottom of a wide-mouthed bottle of about 3 liters capacity was covered with glass beads to a sufficient depth to hold in place a large porcelain crucible about 30 x 30 mm. The bottom of the crucible was kept from direct contact with the bottom of the bottle that the latter might not be cracked by local heating. Through the neck of the bottle was passed a gas delivery tube, reaching to the bottom of the bottle, and a wide glass tube, about 30 mm. in diameter, which could be raised before beginning the experiment to assist in driving out air, but lowered almost to the mouth of the crucible when the reagents are to be dropped in. A gas tube was passed into this wide tube and connected by a Y with the same nitrogen apparatus described in the reaction with sodamide and phosphorus pentachloride. By means of pinch-cocks nitrogen could be delivered into the bottom of the bottle, into the vicinity of the reacting substances, or simultaneously through both tubes at will. The stream of nitrogen was not discontinued at the end of the experiment until the apparatus was quite cool. The reaction proceeded with far less vigor in an atmosphere of nitrogen than in air. The heat of a warmed glass rod was sufficient to start the reaction. Precautions had to be employed to prevent too great a rise in temperature, for with such rise much of the phosphorus was converted into the red modification. It has not been found possible to prevent entirely this formation of red phosphorus, but under favorable conditions not much in excess of 1 per cent. of the compound consists of it.

When the air had been displaced, the finely powdered sodamide and the phosphorus in small pieces were dropped through the long tube into the crucible in small successive portions. The phosphorus was dried as thoroughly as possible by absorbent paper or, better, by benzene. The material could not be removed from the atmosphere of nitrogen before it had become cool nor subjected to any friction without danger of spontaneously inflaming. It was, therefore, moistened with carbon disulphide when cool, removed to a mortar, pulverized under the same liquid and freed from excess of phosphorus by repeated washing in carbon disulphide, which had been dried over calcium chloride.

The attempt was made to remove any excess of sodamide which it might contain by washing with absolute alcohol, but it was found that the entire compound was broken down with evolution of phosphine. In fact, even the treatment with carbon disulphide was observed to set free appreciable amounts of ammonia and of phosphine, and this was taken as a significant indication of the presence of certain unstable components of the reaction. The purified powder was dried at the ordinary temperature in an atmosphere of nitrogen, transferred to tightly stoppered containers and placed in a phosphorus pentoxide desiccator.

Properties.—The chocolate-red powder thus obtained is sensitive to traces of moisture and gives off continually a disagreeable odor suggestive of garlic. In the air it rapidly deliquesces and becomes lighter in color. When heated in air it gives off ammonia and phosphine, while the sodium salts of hypophosphorous and phosphorous acids remain. Heated in a supply of dry carbon dioxide gas it gives off the two gases above and there remain sodium carbonate, hypophosphite and phosphite. Water, dilute acids and alcohol break it down in the same way, but if alcohol is used, the phosphine is not inflammable. Hydrogen is also evolved in considerable quantity by decomposition with water or acids. Absolute ether, chloroform or benzene are without apparent action on the compound.

Historical.—Before entering upon the analysis or constitution of this compound brief reference must be made to work which has been done along similar lines. Gay-Lussac and Thénard, and also Davy supposed that phosphides of the alkali metals could be formed by heating the elements together in nitrogen.

In 1829, Magnus[1] devised a method for the preparation of potassium phosphide, K_3P, which was later used by Vigier[2] in preparing the similar sodium phosphide. Phosphorus was melted under petroleum (boiling-point 120°) and bits of potassium were added from time to time. The oil was distilled off, the excess of phosphorus removed by carbon disulphide and the residue dried at a low temperature in a current of dry carbon dioxide. He stated that the compound separated carbon as well as phosphine when treated with water or dilute acids, and that he was not able to get the phosphide in a state of purity. Vigier's sodium

[1] Pogg. *Ann.*, **17**, 527.
[2] *Chem. News*, 1861, p. 273.

phosphide was described as a black compound. In the course of this work his experiments were repeated, resulting in the verification of his method and description, and, in addition, a partial analysis was made. Vigier used his phosphide in an organic research and he made no attempt to analyze it. Magnus gives nothing but the formula for his potassium phosphide, making no statement as to any analyses upon which he based his conclusions. Rose[1] caused potassium and phosphorus to combine in a flask in the presence of hydrogen. At the end of the experiment the excess of phosphorus was distilled off. He obtained a crystalline mass of the color of "japanned copper."

Bunsen[2] showed that sodium phosphide was formed by heating sodium and sodium phosphate together in a tube and he recommended this as a qualitative method in testing for the presence of phosphorus. Sodammonium, $NaNH_3$, and potassammonium, RNH_3, have, in the hands of Hugot and Joannis, working independently, been of considerable importance. Sodammonium in excess, red phosphorus and sodium, left in contact for several days, formed $P_2H_3Na_3$ ($Na_3P.PH_3$), sodamide and ammonia. The phosphide is described as a yellow crystalline body yielding phosphine in the presence of moisture.[3] The authors claim that if the red phosphorus is in excess $P_5K.3NH_3$ is formed, which loses its ammonia at 180°. It is always more or less contaminated with potassamide. With sodium $P_3Na.3NH_3$ is formed, becoming P_3Na at 180°.[4] If no sodium (or potassium) is used, or if phosphine be led into sodammonium or potassammonium, the substituted phosphines $NaPH_2$ and KPH_2 are formed.[5]

The chemistry of the phosphides of hydrogen is also closely interwoven with this work, because the phosphine produced was relied upon as a measure of the amount of sodium phosphide in the compounds analyzed. It was Thénard[6] and, later, Gatterman,[7] who first separated and determined the constitution and properties of gaseous, liquid and solid phosphines. The former also noted the presence of free hydrogen in ordinary phosphine.

[1] Pogg. *Ann.*, **12**, 547.
[2] *Ann. Chem.* (Liebig), **138**, 292.
[3] *Compt. Rend.*, **127**, 553, and **126**, 1719.
[4] *Ibid.*, **121**, 206.
[5] *Ibid.*, **119**, 557.
[6] *Ann. Chem.* (Liebig), **55**, 27.
[7] *Ber. d. chem. Ges.*, **23**, 1174.

Hoffman[1] showed that in all the common methods of producing phosphine the gas was diluted with from 6 to 80 per cent. of hydrogen (volumetric). When phosphine was made in the ordinary way, by heating an aqueous solution of potassium hydroxide with yellow phosphorus, only from 10 per cent. to 40 per cent. of the gas obtained was phosphine. Alcoholic potash gave about 45 per cent. phosphine. If calcium phosphide was used, the yield of phosphine was better, but was far from pure. The amount of hydrogen formed was very changeable. Even the decomposition by heat of pure phosphoric acid yielded a phosphine which contained at least 6 per cent. of hydrogen. The decomposition of pure phosphonium iodide, PH_4I, is the only method of obtaining pure phosphine. He also showed that fuming nitric acid, as well as the vapor of chlorine and bromine, render non-inflammable phosphine self-inflammable.

Bodroux[2] pointed out that temperature had something to do with the amount of hydrogen produced; in the case, at least, of the decomposition of certain phosphides. When aluminum or magnesium phosphides are decomposed with water they yield phosphine slowly. If the water be above 50° or if acids are used, much hydrogen is developed; if ice-water is used, no hydrogen is formed.

Analysis. Volumetric Gas Determination.—The powdered compound was decomposed by water or by acids in the apparatus described for the examination of sodamide (see Figs. 2 and 3) in an exactly similar way. The atmosphere of carbon dioxide prevented the phosphine from inflaming, although the reaction was violent and a great amount of heat was liberated. The solution remaining in the generator *A* was strongly alkaline, responded to the tests for hypophosphorous acid and contained a small amount of red phosphorus.

The volume of the gases remaining in the burette after the absorption of the ammonia and the carbon dioxide was noted and they were then passed into a Bunsen gas pipette filled with a freshly prepared solution of cuprous chloride in concentrated hydrochloric acid to absorb the phosphine. Measured portions of the unabsorbed gas remaining were then transferred to a eudiometer and exploded over mercury with electrolytic oxygen.

[1] *Ber. d. chem. Ges.*, **4**, 200.
[2] *Bull. Soc. Chim.* (3), **27**, 568.

Portions made at different times showed a variation in composition, and analyses of the same material at widely different periods further showed deterioration to be continuous. In the preparation of the first portion sodamide was used in excess, which was known to yield considerable nitrogen when decomposed by water. In the other two portions excess of phosphorus was used. Only a few representative data are given:

Portion 1.—

0.8664 gram of the material yielded 23.7 cc. of gases, of which 47 per cent. was phosphine, 45.7 per cent. hydrogen, and 7.2 per cent. nitrogen.

1.1614 grams (analyzed later) yielded 35.9 cc. of gases, of which 46.8 per cent. was phosphine, 46.1 per cent. hydrogen, and 7.1 per cent. nitrogen.

0.6109 gram yielded 19.5 cc. of gases, of which 46.8 per cent. was phosphine, 44.4 per cent. hydrogen, and 8.7 per cent. nitrogen.

Portion 2.—

0.9043 gram yielded 69 cc. of gases, of which 28.1 per cent. was phosphine, 71.8 per cent. hydrogen, and no nitrogen.

0.6764 gram (analyzed later) yielded 59.9 cc. of gases, of which 19.9 per cent. was phosphine, 80.1 per cent. hydrogen, and no nitrogen.

Portion 3.—

0.4126 gram yielded 57 cc. of gases, of which 16.15 per cent. was phosphine, 83.8 per cent. hydrogen, and no nitrogen.

0.4765 gram (analyzed later) gave 67.3 cc. of gases, of which 14.8 per cent. was phosphine, 85.1 per cent. hydrogen, and no nitrogen.

Although Bodroux[1] had shown temperature to be a controlling factor in the amount of hydrogen obtained from aluminum and magnesium phosphides, it was found in similar experiments with the sodium phosphide, made by the method of Vigier, that only a slight change could be detected.

0.2987 gram, decomposed by water at 20°, yielded 39.01 per cent. phosphine, the remaining percentage being hydrogen.

0.3467 gram, decomposed by water at 0°, the generator being immersed in ice-water, yielded 40.84 per cent. phosphine. It will be remembered that Bodroux obtained no hydrogen when he used ice-water.

[1] *Loc. cit.*

Ammonia was determined by two methods:

(1) A weighed portion of the compound was placed in a small weighing bottle and lowered into a pressure bottle containing some six-normal hydrochloric acid. The top was adjusted and the apparatus was set away for twenty-four hours for the vapor of the acid to slowly attack the compound. At the end of that time substance and acid could be intimately mingled without development of dangerous pressures. The contents of the bottle were then distilled with excess of sodium hydroxide into a standard acid and the liberated ammonia determined in the usual way by means of titration.

0.2418 gram of the compound gave 22.49 per cent. of ammonia.

(2) A second weighed portion was placed in a small U-tube and hydrochloric acid gas was forced or drawn over it and then through two U-tubes containing dilute sulphuric acid. The dilute acid itself was finally brought into contact with the substance by rapidly boiling the hydrochloric acid. The contents of the three U-tubes were then proceeded with as above.

0.4434 gram of the compound gave 22.8 per cent. of ammonia.

Gravimetric Determinations.—Sodium was determined gravimetrically as sulphate. The phosphorus was removed by oxidation with nitric acid, precipitation by lead acetate and lead carbonate, and after filtration from the phosphates, excess of lead was removed by hydrogen sulphide.

0.4627 gram of compound gave 0.6313 gram of sulphate, equal to 44.22 per cent. Na.

0.1559 gram of compound gave 0.2098 gram of sulphate, equal to 43.63 per cent. Na.

The determination of phosphorus was made in a pressure bottle with fuming nitric acid, the preliminary details being after the manner described for the absorption of ammonia. Fuming acid was used because it was certain that it would oxidize every trace of phosphine and complete the oxidation to phosphate of any lower oxygen compounds of phosphorus. The action within the pressure bottle was usually violent. In from one to two hours after closing the bottle an explosion with flame, of sufficient force to shatter the weighing glass within which was contained the substance, usually occurred within the bottle. After the lapse of several hours the bottle was gently heated in a water-bath without removal of the stopper, to complete the oxidation of all traces of

volatile phosphorus compounds. The bottle was then opened and its contents evaporated on the water-bath almost to dryness. The phosphorus was determined as magnesium pyrophosphate. The determination was verified by first precipitating a second portion to be analyzed with ammonium molybdate and then with magnesia mixture.

In the third determination, to show that there was no conversion of the phosphates into metaphosphates, the solution was boiled with a large excess of water for thirty hours, the water lost by evaporation being restored from time to time. The results reached in all these methods agreed well within the limits of experimental error.

0.2496 gram of compound gave 0.1476 gram magnesium pyrophosphate, or 16.46 per cent. phosphorus.

0.1637 gram of compound gave 0.0968 gram magnesium pyrophosphate, or 16.45 per cent. phosphorus.

0.1750 gram of compound gave 0.1064 gram magnesium pyrophosphate, or 16.91 per cent. phosphorus.

Reactions and Composition.—(1) It has been shown by analytical results that successive preparations do not possess the same composition.

(2) The products of its decomposition by water or acids are numerous. Phosphine, hydrogen, ammonia, sodium hypophosphite, sodium hydroxide, and red phosphorus have been detected and there is much reason for believing that salts of phosphorous and of phosphoric acids are also formed. There is no one salt of definite composition which can be conceived to be formed by these two reagents capable of yielding all these products simultaneously in the proportions found.

(3) It has been shown that the instability of the compound in the presence of air, heat, and the common solvents is very great, while, on the other hand, the common organic solvents, alcohol excepted, are, if dry, without action upon any of its constituents. Owing to these facts the attempt to purify the compound or to isolate any of its constituents has met with no success.

(4) Sodamide may break down in the presence of substances capable of uniting with it in either one of two ways. Thus, as in the union with water, the point of rupture in the sodamide is between the sodium and the amido group. On the other hand,

as Titherly[1] has shown, when sodamide reacts with many organic compounds, especially the organic amides, an amido hydrogen atom is substituted by the organic residue.

(5) The behavior of phosphorus is even more anomalous. The long list of phosphorus compounds, prepared by chemists from the time of Magnus and Rose to the present, show clearly that the distribution of the valencies of phosphorus toward groups with which it is capable of uniting lead to no certain generalizations. To a certain extent, but in a less degree, phosphorus resembles carbon in the formation of the complex chains. Vigier's compound has had ascribed to it the formula Na_3P, but it certainly contains a considerable portion of Na_4P_2, for its phosphine is very inflammable.

In view of all these facts the reaction between phosphorus and sodamide in the presence of an inert gas may be supposed to take place in any of the following ways:

(1) Assuming sodamide to break down into sodium and amidogen,

$$(a) \quad 2P + 6NaNH_2 = 2Na_3P + 4NH_3 + N_2.$$
$$(b) \quad 2P + 3NaNH_2 = Na_3P + (NH_2)_3P.$$

(2) Assuming sodamide to substitute phosphorus for hydrogen in the amide group,

$$(c) \quad P + 3NaNH_2 = (NaNH)_3P + 3H.$$
$$(d) \quad 2P + 3NaNH_2 = (NaN)_3P_2 + 6H.$$

Two methods were employed in the attempt to determine which of these reactions occur:

(1) Analysis of the products of decomposition.

(2) To conduct the synthesis of the compound in such a manner that the evolved gases, if any, may be collected and their nature and amount determined. The solution of this problem would be relatively easy, if the compound were not a mixture of such great instability.

In the prosecution of the first method it was ascertained that the compound contains sodium hypophosphite through the action of the sodium hydroxide, always found in sodamide in amounts varying from 1 to 10 per cent. upon the excess of phosphorus. The reaction is

[1] *J. Chem. Soc.* (London), **71**, 460.

$$6NaOH + 4P = 3NaH_2PO_2 + Na_3P.$$

Red phosphorus is also always formed in amounts varying from 0.25 to 1.5 per cent., according to the temperature of the reacting mass and the proportion of the constituents. Inability to exclude air and moisture completely also insures the presence of other oxygen acids of phosphorus.

The analysis to determine the products of decomposition was carried on in three ways:

(1) Volumetrically, as already described, whereby the proportion of phosphine and of hydrogen was determined.

(2) Qualitatively, to show the presence of sodium hydroxide and of the salts of the acids of phosphorus.

As is well known, the recognition of hypophosphorous, phosphorous and phosphoric acids when all three are present in the same solution is a difficult matter. The presence of hypophosphorous acid could be assumed in view of the reaction between sodium hydroxide and phosphorus given above. The fresh solution also reduces potassium permanganate immediately, as do hypophosphites. The decomposition of sodium phosphide by water also yields sodium hypophosphite, as was proven by examination of the solution obtained by decomposing Vigier's sodium phosphide with water. But that phosphorous or phosphoric acids, or both, are also present is shown by the fact that after neutralization of the sodium hydroxide with acetic acid the addition of lead acetate solution gives a white precipitate, whereas lead hypophosphite is soluble in acetic acid. When ammonium molybdate is added to the solution, freshly obtained by decomposing the compound with water, a blue coloration was observed which, on standing or gentle warming, became colorless, and with the addition of a drop or two of nitric acid, well diluted, and gentle heat, the usual ammonium phosphomolybdate precipitate, indicative of phosphoric acid, was obtained.

Knowing the energetic reducing properties of hypophosphorous acid, it was at first thought that the blue color was due to reduction of the molybdic anhydride to the sesquioxide by the hypophosphorous acid, and that this could advantageously be used as a qualitative test for the presence of this acid. But when pure hypophosphorous acid was prepared free from traces of phosphine no such reduction occurred. When it is recalled that phosphine

is even more energetic as a reducing agent than hypophosphorous acid, and that phosphine is, to some extent, soluble in water and more so in a strong solution of sodium hydroxide, the reduction of the molybdic anhydride must be ascribed to the presence of phosphine. To confirm this observation it is known that phosphorous acid, reduced with nascent hydrogen, yields phosphine and hypophosphorous acid, and when ammonium molybdate solution is added to this reduction product of phosphorous acid the blue coloration is observed.

(3) Quantitatively, to determine how much of the phosphorus in the original compound went to the formation of phosphine and how much to the formation of oxygen or other compounds of phosphorus. The compound was decomposed by alcohol to prevent ignition of phosphine, the oxidation products of which would be dissolved in the liquid and vitiate the results. The solution was boiled to expel the phosphine, oxidized with nitric acid and the phosphorus precipitated with magnesia mixture.

0.1418 gram of compound gave 0.042 gram magnesium pyrophosphate, corresponding to 8.24 per cent. phosphorus.

As the total phosphorus obtained from the compound was 16.68 per cent., it is seen that the result of this experiment indicates that half of the phosphorus of the compound disappears as phosphine, and the other half remains in solution as a salt of one or more of the acids of phosphorus.

The synthesis of the compound was carried on by the aid of the apparatus described in Fig. 2. In the bottom of the generator, *A*, was placed a small cup of sheet aluminum to protect the apparatus from breaking in the heat generated by the reaction. After filling the apparatus with dry carbon dioxide, about 0.4 gram of phosphorus dried by benzene and approximately 0.7 gram of powdered sodamide were dropped into the cup and carbon dioxide was again passed through for some time. No combination took place in the presence of this inert gas at ordinary temperatures. The Hempel's burette, filled with sodium hydroxide solution, was attached after introducing into it a measured small portion of oxygen to act as a gas cushion. On gentle heating under diminished pressure, a quantity of gas was forced over, most of which was absorbable. After the generator had cooled to the normal temperature dry benzene (which does not decompose the compound) was admitted through the funnel and all the gas driven

into the burette. After thorough shaking the gas volume was read. Deducting for the oxygen there was a remainder of 7.58 cc. This gas was transferred to a eudiometer, exploded over mercury with a known excess of oxygen, the oxygen remaining absorbed by potassium pyrogallate solution and the remainder calculated as nitrogen. The results which, of course, are merely approximate, show that both nitrogen and hydrogen are liberated in the reaction, the latter being in slight excess. Since ammonia is also formed, the two equations which best accord with these conditions are (*a*) and (*c*), page 1506. Thermometric measurements of the temperature at which combination of phosphorus and sodamide takes place are of little value. The heat evolved is sudden and ephemeral. Reaction began at 150°, or about the melting-point of sodamide and in a few seconds rose to nearly 250° (uncorrected).

The invariable presence of hydrogen among the gases formed calls for explanation and in regard to the formation of this no information could be obtained from the published work of those who had investigated the compounds of phosphorus and hydrogen.

For the formation of phosphine in the usual way from phosphorus and potassium or sodium hydroxide, heated together, the following equation is usually given:

$$4P + 3KOH + 3H_2O = PH_3 + 3KH_2PO_2.$$

Without doubt the reaction is far more complicated, and for the sake of clearness may be assumed to take place in the following stages:

(*a*) $4P + 6KOH = 2K_3P + 2P(OH)_3.$

(*b*) $2K_3P + 7H_2O = PH_3 + KH_2PO_2 + 5KOH + 4H.$

(*c*) with excess of KOH, as is always the case,

$$2P(OH)_3 + 4KOH = 2K_2HPO_3 + 4H_2O.$$

Whence by combination of these three and reduction to simplest terms there remains the completed equation:

(*d*) $$4P + 5KOH + 3H_2O = PH_3 + KH_2PO_2 + 2K_2HPO_3 + 4H.$$

The presence of a higher oxidation product than hypophosphorous acid can be shown by the method already given. In a

similar way while we might expect a compound of the formula Na_3P to unite with water thus:

$$Na_3P + 3H_2O = PH_3 + 3NaOH,$$

the analyses show that more complex changes occur, probably represented by

$$4Na_3P + 14H_2O = 2PH_3 + NaH_2PO_2 + Na_2HPO_3 + 9NaOH + 10H;$$

and to account for the inflammable phosphine, traces of the sodium salt of which are undoubtedly present,

$$2Na_3P_2 + 10H_2O = P_2H_4 + NaH_2PO_2 + Na_2HPO_3 + 5NaOH + 8H.$$

Reference should be made here to the occurrence of ammonia-nitrogen in the compound. Analysis yields 22.64 per cent. NH_3, equivalent to 21.3 per cent. NH_2. That this is not present as unchanged sodamide is definitely known from:

(1) The appearance of the compound before pulverizing it—its uniform color showing it to be quite homogeneous.

(2) This amount of NH_2 would demand over 51 per cent. of the compound to be sodamide, of which 30.58 per cent. would be sodium. The absence of free nitrogen from the gases obtained by decomposition is, of itself, proof of the absence of sodamide. But further, if, as has been shown by analyses, the amount of phosphorus in phosphine represents one-half of the phosphorus present in the form of sodium phosphide there would, on this basis, be 19.29 per cent. sodium phosphide. Of this, 13.32 per cent. would be sodium, and thus to assume sodamide present in the per cent. mentioned would, for these two compounds, require all of the sodium and all of the ammonia-nitrogen, leaving 13.7 per cent. of phosphorus unprovided for. It is justifiable, therefore, to assume some substituted amide of phosphorus to be present analogous to the substituted amides of organic compounds, described by Titherly. It could hardly be surmised that any ammonium compounds were formed. In the presence of other constituents of this compound it is impossible to say how such compounds would break down.

Sodamide as a Reagent.—Sodamide lends itself very readily to synthetical operations, and the only drawback to its use is the difficulty of obtaining it in the pure condition. Its use is also

further hampered by the difficulty of separating the by-products from the end-products desired. This is well illustrated by the present work. Sodamide affords a quick method for the preparation of impure phosphine and a number of its by-products have led into interesting theoretical discussions. Much work remains to be done with sodamide in the field of inorganic chemistry. While in the present instance the reaction is not a clean-cut one, it would be unfair to assume that with elements not so closely related, according to our present views of the periodic system, as are phosphorus and nitrogen, results of a far more satisfactory character will not be gained.

FINAL SUMMARY.

Sodamide.—

(1) Yields hydrogen and nitrogen in varying amounts when decomposed by water.

(2) Hydrogen can be almost completely eliminated

(*a*) By prolonged heating at high temperatures with excess of NH_3.

(*b*) By long standing in closed bottles.

(3) Nitrogen is always present and is very probably due to sodium triazoate or some analogous compound, the formation of which in sodamide is due to partial oxidation of ammonia, as pointed out

(*a*) In process of manufacture of sodamide.

(*b*) By long standing in presence of dry air.

(4) Occurrence of nitrous and hyponitrous acids in sodamide that has become yellow through exposure to dry air.

(5) Formation of disodium cyanamide in the wet way.

Sodamide and Phosphorus Pentachloride.—

(1) Formation of an insoluble compound which cannot be isolated from the products formed along with it without undergoing change.

(2) When thus separated by nitric or acetic acids and analyzed it is found to correspond to the formula PO_2N, or PONHOH.

Sodamide and Yellow Phosphorus.—

(1) Forms a complex compound containing sodium phosphide along with other products (probably an amide of phosphorus), oxygen acids of phosphorus, etc.

(2) Pressure bottle method of decomposition and analysis for explosive or volatile compounds capable of decomposition at temperatures below the boiling-point.

(3) Elaboration of methods for simultaneous recognition of hypophosphorous, phosphorous and phosphoric acids.

(4) Discussion of the source of hydrogen in the preparation of phosphine.

(5) Qualitative test for phosphine by ammonium molybdate.

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VOLATILIZATION OF PLATINUM.

By G. A. HULETT AND H. W. BERGER.

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IN DETERMINING the effect of heat on barium sulphate[1] we observed a decrease in the weight of the platinum dish used. Heated to 1125° C. for four hours in an electric furnace there was a loss of 1.4 mg. and a platinum mirror was deposited on the cover of the furnace.

In 1852, Deville observed that noticeable amounts of platinum collected on the cover of the furnace in which he melted his platinum. Deville suggested that this might be due to volatilization. Aitken,[2] in 1879, in studying the formation of fog, observed that a platinum spiral glowed by an electric current gave off particles which produced a fog in an otherwise dust-free but moist atmosphere. The so-called "Zerstäubung" of electrically glowed platinum wires and points has been frequently observed, also that a metallic mirror is deposited on colder objects in the vicinity of the glowing wire. R. Nahrwold[3] paid particular attention to this phenomenon and was able to show that no "Zerstäubung" took place in an atmosphere of hydrogen or in a vacuum. It was necessary for oxygen to be present in order that the platinum wire lose weight when glowed by an electric current. Further evidence of the same nature has been obtained by W. Stewart,[4] and more particularly Holborn and Henning,[5] and Hol-

[1] *Zischr. anorg. Chem.*, **40**, 209 (1904).
[2] *Nature*, **31**, 268.
[3] *Wied. Ann.*, **35**, 116 (1888).
[4] *Ibid.*, **66**, 88 (1898).
[5] *Sitzungsber. Berl. Akad.*, 1902, p. 936.

born and Austin,[1] have shown that platinum, iridium and rhodium all show this phenomenon. It is most marked with iridium, but it is only in oxygen or mixtures of gases that contain oxygen that the electrically glowed wire loses in weight and deposits the metal on colder objects. Palladium seems to behave differently from the others, losing weight independently of the gas and noticeably in vacuum. Palladium thus shows a true volatilization. The temperatures used by the above investigators ranged from 1050° C. to 1500° C.

We have made a few more experiments with the electric furnace, using a sheet of platinum foil 19.4 by 13.6 cm. wound in a loose coil so that it could be suspended in the heating cylinder of the electric furnace and also so that a slow current of air, free from carbon dioxide, might pass up through the coil. The total surface was some 530 sq. cm. We started at 900° C. (the temperature was measured as before)[2] and in two hours we found a loss of 1.6 mg., while we had hardly expected a loss at this temperature. A further two hours' heating at 900° showed a loss of 1.4 mg., and a third two hours' heating at the same temperature showed a loss of 0.9 mg. The foil was next heated for two hours at 1020° and lost 1.5 mg. The foil had now assumed a frosted appearance, such as is observed on platinum, which has been attacked by aqua regia. The foil was now treated with aqua regia until it had lost 220 mg., was rinsed, rapidly glowed, weighed and then heated in the furnace, as before, for two hours at 1020°. The loss was 5.6 mg. This decrease in loss on successive glowings has also been observed by Stewart,[3] and from this last result it seems that on removing the surface layer with aqua regia the subsequent glowing shows a maximum loss. Also burnishing with fine pumice has the same effect as treating with aqua regia, but the subsequent glowings show a decreasing loss for each successive glowing. The foil used was common platinum foil, 0.1 mm. thick, and evidently contained little iridium, as it dissolved completely in aqua regia; however, it seemed desirable to test pure platinum and we turned to the platinum manufactured by Heraeus for thermocouples, which contains no palladium or rhodium, hardly a trace of iridium and only 0.001 per cent. of

[1] *Sitzungsber. Berl. Akad.*, 1903, p. 245.
[2] *Ztschr. anorg. Chem.*, **40**, 209 (1904).
[3] *Loc. cit.*

iron.[1] A short piece of this wire, kindly loaned by Prof. E. D. Campbell, was rolled flat (except the ends) and then glowed in air by a current of 5.15 amperes. The flat portion, which only was at a white heat, was 38 cm. long and 1 mm. wide. Glowed for one-half hour the loss was 0.55 mg. The second half hour gave 0.27 mg. loss, and the third half hour gave 0.5 mg. loss. The ribbon was dipped in aqua regia, losing 0.2 mg. and then glowed, losing 0.8 mg. A current of 5.15 amperes was used for each glowing, but the temperature was probably not the same in all the glowings, as the resistance of the ribbon may have changed. However, the results show that this pure platinum behaves essentially as the foil.

Evidently the volatilization of platinum has little to do with the impurities present, nor are the impurities the cause of the very curious phenomenon of the decreasing losses of the successive heatings. It seems due to some condition of the surface brought about by volatilizaton of the metal and not to a condition of the surface due to a heating and cooling of the metal. The phenomenon presents an interesting problem in itself.

We wished especially to find the lowest temperature at which platinum loses weight. The above foil was, therefore, heated two hours at 810° with a slow air current passing up through the heating cylinder. The loss was 0.13 mg., while a second two hours at the same temperature showed a loss of 0.1 mg. At 870° the loss was 0.6 mg. when heated for two hours. The foil was now treated with aqua regia and then heated for two and one-half hours at 795°, but there was no detectable change in weight. It seems then that 800° is the lowest temperature at which the effect is noticeable. At 900° 100 sq. cm. surface loses about 0.25 mg. per hour as a maximum. At 1000° the loss amounts to 1 mg. per 100 sq. cm. surface.

In exact analyses where precipitates are glowed in platinum it is evidently advisable to check the weight of the platinum vessel used after the operation. The temperature in ordinary analytical work is considerably over 900°, as shown by the following experiment. A platinum crucible, supported by a platinum wire triangle, was provided with a perforated cover. The double-bored porcelain tube of the thermocouple extended through the cover and the junction of the couple rested on the bottom of the crucible.

[1] Mylius and Foerster: *Ber. d. chem. Ges.*, **25**, 683 (1892).

When the crucible was glowed by a good Bunsen flame, we observed a temperature of 960°. On blasting the crucible with foot bellows and lamp 1160° was observed, and now on changing back to the Bunsen burner, 975°. These temperatures are, of course, affected by a good many factors, but give an idea of the temperature ordinarily obtained and they are such that volatilization can very readily take place. The volatilization will depend, however, on the amount of oxygen in the gases immediately in contact with the platinum.

The electric furnace used in our experiments consists of a vertical cylinder 6.5 cm. in diameter and 30 cm. deep. Around this cylinder is wound spirally a platinum foil. This cylinder is surrounded by a second larger cylinder, leaving an air-space of 1.5 cm. Here it will be noticed is an opportunity for the volatilization of platinum during the use of the furnace, for the foil and inner cylinder are at a very high temperature, while the surrounding cylinder is at a much lower temperature. On dismantling the furnace it was found that the inside of the outer cylinder presented a glistening appearance, due to innumerable tiny crystals of platinum. They were brushed off and some 30 mg. recovered, and perhaps as much more lost. Some of these crystals were 200×100 μ $=(0.2 \times 0.1$ mm.) and many well formed ones were 80 μ in diameter.

Platinum then begins to volatilize in air at about 800° C. where the effect is just perceptible and the rate increases markedly with the temperature. *In vacuo* or in an oxygen-free atmosphere there is no volatilization. The phenomenon is then due to the presence of oxygen and it seems probable that there are volatile compounds of the platinum metals which are stable at high temperatures, but decompose at lower temperatures, and such compounds would probably be endothermic. The existence of a volatile oxide of platinum which decomposes at 800° and below, but is stable above that temperature would account for all of the observed facts. The sprouting of molten platinum, when cooling, might well be due to the presence in solution of such a compound and as the temperature decreases decomposition takes place, with liberation of oxygen. The detection of compounds, which exist only at high temperatures, offers an interesting problem.

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SOME TRI-*p*-TOLYLMETHANE DERIVATIVES.

By N. E. Tousley and M. Gomberg.

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Two tritolylmethanes are mentioned in the literature. Rosenstiehl and Gerber[1] obtained, by the reduction of a rosaniline dye of the composition $C_{22}H_{25}N_3O$, a crystalline compound melting at 73° C., which they describe as tri-*m*-tolylmethane. Later Elbs and Wittich[2] found that the condensation of chloropicrin, CCl_3NO_2, with toluene, by means of aluminium chloride, does not proceed as smoothly as that with benzene. They have, however, obtained, by the fractional distillation of the resulting mixture, a body which boiled above 360° and remained viscous at —10°, and which they consider as tritolylmethane, or a mixture of such isomers. The position of the three methyl groups has not been determined by them. Gomberg and Vödisch[3] showed that carbontetrachloride, analogously to chloroform, does not condense with toluene as readily as it does with benzene. While the yield of triphenylchlormethane is 90 to 95 per cent. of the theoretical amount, in the case of the tritolyl compound it is at best 20 to 30 per cent. We have now definitely established the constitution of this body as a *p*-tritolyl derivative and, with the chloride as a starting-point, we have also studied some other derivatives of tri-*p*-tolylmethane.

Tri-p-tolylchlormethane.—To a mixture of 350 cc. carbontetrachloride, 700 cc. toluene and 1000 cc. carbon disulphide, 350 grams of aluminium chloride were added in small amounts, the addition extending over two or three days. When the reaction, which proceeded at room temperature, had ceased the mixture was poured into ice-water to break up the compound with aluminium chloride. The carbon disulphide solution was then saturated with dry hydrochloric acid gas in order to convert any tritolylcarbinol formed back into the chloride, and dried over calcium chloride. On distilling off the carbon disulphide, tritolylchlormethane separated in yellow crystals. The crystals were filtered off by means of suction and washed with petroleum ether. One hundred and fifty grams of the recrystallized product were obtained, which represents a yield of 32.8 per cent. of the calculated amount. The condensation of carbontetrachloride with toluene at higher

[1] *Ann. chim. phys.* [6], **2**, 353, 368 (1884).

[2] *Ber. d. chem. Ges.*, **18**, 347 (1885).

[3] **This Journal**, **23**, 177 (1901).

than ordinary room temperature gives much smaller yields of the tritolylchlormethane. Attempts to substitute ferric chloride in place of aluminium chloride gave unsatisfactory results. The chloride dissolves readily in benzene, ether and carbon disulphide, and may be recrystallized from cold acetic ether or petroleum ether, in which it is but slightly soluble. It melts usually at 165° to 168°, but when perfectly pure it shows a melting-point of 173°. An estimation gave 10.99 per cent. of chlorine; calculated, 11.06 per cent.

The molecular weight was determined by the freezing-point method in benzene. 0.5601 gram substance in 18.461 grams benzene gave a depression $\Delta = 0.500°$. This corresponds to a molecular weight of 303.5; calculated, 320.5.

Synthesis by Means of Grignard's Reaction.—The constitution of the above chloride as a *p*-tritolyl-compound, follows from the synthesis of the identical compound from *p*-tolyliodide and *p*-toluic ethylester, by means of Grignard's reaction. *p*-Tolyliodide and *p*-toluic acid were both prepared from pure *p*-toluidine. The *p*-toluic acid was converted into *p*-toluic ethylester by heating with alcohol and sulphuric acid.[1] Fifty grams of the *p*-tolyliodide, 4.8 grams magnesium and 60 grams absolute ether were heated on the water-bath until the magnesium had gone into solution. To this solution of the *p*-tolylmagnesiumiodide compound 18 grams *p*-toluic ethylester, in an equal amount of absolute ether, were then gradually added through a dropping funnel and the mixture heated two hours on the water-bath. Ice-water was then added to decompose the magnesium compound, and the ether and excess of *p*-tolyliodide were driven off by distillation with steam. The carbinol remained in the distillation flask as a dark viscous mass which refused to crystallize. It was dissolved in ether, the solution dried over calcium chloride and saturated with dry hydrochloric acid gas, in order to change the carbinol into *p*-tritolylchlormethane. On concentrating the solution the chloride separated in almost colorless crystals, melting at 164°. To estimate the chlorine, the substance was dissolved in warm, concentrated sulphuric acid, and the escaping hydrochloric acid fumes were led into a solution of silver nitrate and weighed as silver chloride.[2] This gave 11.4 per cent. chlorine; calculated, 11.06 per cent.

[1] *Ann. Chem.* (Liebig), **63**, 295.
[2] *Ber. d. chem. Ges.*, **35**, 2400 (1902).

The product was found to be identical in every respect with that obtained by the Friedel-Crafts reaction from carbontetrachloride and toluene.

Tri-p-tolylcarbinol, $(CH_3C_6H_4)_3COH$.—The carbinol was prepared from the chloride by dissolving the latter in a mixture of equal parts of sulphuric and acetic acids, and gently heating the mixture on the water-bath in order to drive off the hydrochloric acid. On the addition of ice-water the tri-*p*-tolylcarbinol was precipitated in coarse crystals. They were purified by recrystallization from petroleum ether. The carbinol is soluble in ether, alcohol, benzene and carbon disulphide, but only slightly soluble in petroleum ether, from which it crystallized in large, colorless crystals, melting at 94°. The analysis gave: C, 87.22; H, 7.44. Calculated for $(CH_3C_6H_4)_3COH$: C, 87.36; H, 7.34.

A molecular weight determination by the freezing-point method in benzene gave the following results: 0.8994 gram substance in 16.012 grams benzene gave a depression $\Delta = 0.952°$. This corresponds to a molecular weight of 291.9; calculated, 302.2.

Attempts to prepare tri-*p*-tolylphenolmethane, according to the method of Baeyer and Villiger,[1] were without results. Five grams of the carbinol and 15 grams of phenol were dissolved in a mixture of 100 grams acetic and 25 grams sulphuric acid. The solution was allowed to stand two weeks, but no condensation took place between the carbinol and the phenol. The experiment was repeated, using 25 grams acetic and 100 grams sulphuric acid. After standing five weeks the solution was poured into water and gave only unchanged carbinol.

Ethoxy Derivative, $(CH_3C_6H_4)_3COC_2H_5$.—Five grams of the tritolylchlormethane and slightly more than the theoretical amount of sodium ethylate, in absolute alcohol, were heated one hour under a reflux condenser. The solution was then cooled, filtered from the precipitated sodium chloride and concentrated. On standing a short time the pure ethyl ether of tri-*p*-tolylcarbinol crystallized out in fine, white, needle-shaped crystals. When recrystallized from petroleum ether the pure substance melted at 111° C. The yield was 4 grams. The analysis gave: C, 87.20; H, 7.80. Calculated for $(CH_3C_6H_4)_3COC_2H_5$: C, 87.20; H, 7.95.

Action of Acetyl Chloride.—It has been shown, in a previous paper,[2] that when the corresponding triphenylcarbinolether is

[1] *Ber. d. chem. Ges.*, **35**, 3018 (1902).

[2] This Journal, **24**, 618 (1902); **25**, 1271 (1903).

treated with acetylchloride triphenylchlormethane is formed, and not the acetyl derivative, as has been reported by others.[1] With tritolylcarbinolether the result is analogous. The ethoxy compound dissolved readily in acetyl chloride with a slight evolution of heat and, on cooling, precipitated in small white crystals, which were washed with petroleum ether and carefully dried. The substance melted at 173°, showing it to be the pure chloride. Tritolylcarbinol was also treated with acetyl chloride. It dissolved quickly with a strong evolution of heat, and precipitated at once as the chloride, melting at 167°. On recrystallizing from petroleum ether the melting-point rose to 170°.

Tri-p-tolylbrommethane, $(CH_3C_6H_4)_3CBr$.—The action of hydrobromic acid on a solution of tritolylcarbinol is exactly analogous to that of hydrochloric acid. On conducting a stream of the dry gas into a solution of 10 grams of the carbinol in petroleum ether the yellow crystals of the tritolylbrommethane formed at once. The bromide was recrystallized from carbon disulphide by the addition of hot ligroin, in which it is but slightly soluble. Nine grams of the pure compound were obtained. The melting-point of the bromide is 165°. The analysis gave 22.3 per cent. bromine; calculated, 21.9 per cent.

Perhalides of the Tritolylhalogenmethanes.—A perbromide of the above compound was obtained by adding bromine to a solution of tritolylbrommethane in chloroform. A dark red oil separated from the solution and, on cooling, gave orange-red crystals of a perbromide, probably tritolylbrommethane pentabromide, as it contained 58 per cent. of "perbromine" (calculated 52.3 per cent.), as found by titration with sodium thiosulphate in presence of potassium iodide. The perbromide melted at a low temperature and it was found difficult to obtain it sufficiently pure for analysis. The tritolylcarbinolbromide, like the corresponding triphenyl compound, forms periodides. A solution of iodine in carbon disulphide was carefully added to a solution of tritolylbrommethane in the same solvent. The periodide crystallized at once in dark blue metallic-looking crystals, melting at 118° to 120°. Several analyses of the "periodine," by titration with sodium thiosulphate, showed that either the tetra- or the penta-iodide were formed, according to the conditions of the experiment.

[1] *Ann. Chem.* (Liebig), **227**, 116 (1885).

When a solution of tritolylcarbinol is treated with dry hydrochloric or hydrobromic acids the corresponding chloride or bromide is formed. With hydriodic acid, however, a periodide of tritolyliodomethane, melting at 138°, was formed. The action of the hydriodic acid consists in changing some of the carbinol into the iodide, while another part of the carbinol is reduced to the tritolylmethane, whereby an equivalent of free iodine is liberated from the hydriodic acid. The iodine so formed combines with the tritolylcarbinol iodide to give rise to a periodide of variable composition. The pentaiodide was obtained by dissolving 2 grams of tritolylcarbinol and 5 grams of iodine in carbon disulphide, and saturating the solution with dry hydriodic acid. The dark, iridescent crystals were washed with benzene and dried in a vacuum desiccator. The melting-point was 77°. The analysis gave 60.99 per cent. iodine; calculated, 60.66 per cent.

Tri-p-tolylmethane, $(CH_3C_6H_4)_3CH$.—This compound was obobtained by the reduction of the chloride with zinc and acetic acid.[1] Ten grams of tritolylchlormethane were dissolved in 40 cc. acetic acid, and the solution was warmed gently. After displacing the air in the flask with carbon dioxide (to avoid the formation of the tritolylperoxide) 10 grams of zinc dust were added. The solution was kept at 50°, adding more zinc from time to time. A large excess of water was then added, the precipitated hydrocarbon extracted with ether and the solution dried. On distilling off the ether the tritolylmethane was obtained as a thick yellow oil. It distilled almost colorless at 260° to 262° under 28 mm. pressure. The analysis gave: C, 92.43; H, 7.90. Calculated for $(CH_3C_6H_4)_3CH$: C, 92.23; H, 7.76.

The molecular weight was determined by the freezing-point method in benzene. 0.4669 gram substance in 20.0708 grams of benzene gave a depression $\Delta = 422°$. This corresponds to a molecular weight of 267.1; calculated, 286.2.

Oxidation of the Tri-p-tolylcarbinol.—To a solution of 48 grams chromic acid in 72 grams acetic acid were added 12 grams tritolylcarbinol. The solution was heated three hours on the water-bath. A solid green mass separated in the bottom of the flask. This was filtered out and dissolved in a hot, 5 per cent. solution of sodium hydroxide. On filtering this solution and acidifying the clear filtrate with hydrochlorc acid a white, flocculent precip-

[1] *Ber. d. chem. Ges.*, **36**, 283 (1903).

itate of the acid was obtained. When filtered, well washed and dried, it was found to be soluble in alcohol, benzene and acetic acid; insoluble in petroleum ether. But from none of these solvents could it be obtained in crystalline form. By dissolving in sodium hydroxide and carefully neutralizing with acetic or nitric acids the acid could be precipitated either as the lead salt, by addition of lead acetate, or as its silver salt, by adding silver nitrate. Neither of these salts were crystalline. The sodium salt, however, was obtained by the addition of sodium hydroxide to the alcohol solution of the acid. It precipitated in very fine, yellow crystals. An analysis of the sodium salt gave the following results: 14.59 per cent. Na; calculated, 14.53 per cent.

2.5 grams of the acid were then dissolved in potassium hydroxide, precipitated with hydrochloric acid, and carefully washed and dried. The low per cent. of carbon is occasioned by a small amount of potassium retained by the acid. The analysis gave: C, 66.51; H, 4.09. Calculated for $(C_6H_4CO_2H)_3COH$: C, 67.32; H, 4.12.

The acid volatilized slowly, without melting.

Tri-p-tolylaminomethane, $(CH_3C_6H_4)_3C.NH_2$.—It was shown by Nauen[1] that triphenylchlormethane reacts with ammonia to form triphenylaminomethane. In like manner, tritolylchlormethane reacts with ammonia to give tritolylaminomethane. Five grams of the chloride were dissolved in dry, thiophene-free benzene, and the solution was then saturated with dry ammonia gas. Ammonium chloride was formd at once, and after filtering and concentrating the solution the tritolylaminomethane separated in almost white crystals. The pure substance, recrystallized from ether and petroleum ether, melted at 112°. The analysis gave 4.73 per cent. N; calculated, 4.65 per cent.

Tri-p-tolylmethylaniline, $(CH_3.C_6H_4)_3C.HNC_6H_5$.—Tritolylchlormethane reacts also with amines, in like manner to triphenylchlormethane,[2] giving the corresponding substituted tritolylaminomethanes. Five grams of the chloride were dissolved in dry benzene, and to the warm solution 4 grams of aniline were slowly added. Aniline hydrochloride separated at once. After heating gently one hour the solution was filtered and the benzene distilled off. The tritolylmethylaniline compound re-

[1] *Ber. d. chem. Ges.*, **17**, 442.

[2] *Ibid.*, **17**, 703.

mained as a brown viscous mass, soluble in ether, petroleum ether, toluene, etc.; less soluble in acetone, from which it crystallized in fine, white crystals, melting at 64°. The analysis gave 3.55 per cent. N; calculated, 3.71 per cent.

On boiling wth hydrochloric acid tritolylcarbinol is formed. When the aniline compound is heated for some time with alcohol a white crystalline substance was formed, containing no nitrogen, and melting at 111°. This proved to be the ethoxy derivative of tritolylmethane.

Tri-p-tolylmethylparatoluidine, $(CH_3.C_6H_4)_3C.HNC_6H_4.CH_3$.—This compound was made in exactly the same manner in which the aniline derivative was prepared. The yield was small, about half of the theoretical. On recrystallizing from petroleum ether several times the substance was obtained pure, in white crystalline form, and melted at 151°. The analysis gave 3.51 per cent. N; calculated, 3.58 per cent.

Conductivity of the Chlor- and Brom-derivatives.—It has been shown[1] that triphenylchlormethane, when dissolved in benzonitrile, possesses considerable electrical conductivity. The same has been found true in the case of tritolylchlormethane and tritolylbrommethane. Benzonitrile, which has been shown[2] to be a good ionizing solvent for many salts, was carefully dried and fractionated. It showed a specific conductivity of 4×10^{-5} at 20°. On addition of the electrolyte the solution at once assumed a greenish yellow color. The following results were obtained, the temperature being in all cases 20°.

TRITOLYLCHLORMETHANE.

v	1184	375.8	226.7	131.9	88.7	54.4	20.6
μ	1.713	1.023	0.8405	0.6413	0.5126	0.3621	0.2029

TRITOLYLBROMMETHANE.

v	1161	571.9	281.8	107.5	85.59	54.95	21.75
μ	4.515	3.969	2.621	1.611	1.464	1.196	0.7504

The volume in liters containing a gram-molecule is represented by v and the molecular conductivity by μ. It will be observed that the conductivity of the bromide is almost three times that of the chloride. Both compounds show a very measurable conductivity and may be classed, like the corresponding triphenyl derivatives,

[1] *Ber. d. chem. Ges.*, **35**, 2404.
[2] *Ztschr. anorg. Chem.*, **15**, 31; *J. Phys. Chem.*, **3**, 22.

as compounds in the nature of salts. Qualitative tests with liquid sulphur dioxide as a solvent showed a much higher degree of molecular conductivity.

From the experimental results presented in this paper it is seen that tritolylmethane is, in all respects, analogous to triphenylmethane. The presence of so many methyl groups lowers greatly the melting-point of the hydrocarbon, so that even in a freezing-mixture it remains viscous. The two carbinols, those of tritolylmethane and of triphenylmethane, behave similarly toward halogen acids, acetylchloride, reducing agents, etc. The tritolylcarbinol-halides, like the corresponding triphenyl compounds, react readily with water, alcohol, halogens, ammonia and amines. With halide salts, such as mercuric chloride, ferrous chloride and zinc chloride, double salts are formed.[1] Also, as has been shown,[2] they react with zinc and silver in neutral solvents, giving rise to an extremely unsaturated substance, which, on exposure to air, forms tritolylmethyl peroxide, $(CH_3C_6H_4)_3COOC(C_6H_4CH_3)_3$, the reaction being strictly analogous to that of the triphenylhalogen-methanes.

ANN ARBOR, MICHIGAN,
July, 1904.

THE CHEMICAL COMPOSITION OF MAPLE-SYRUP AND MAPLE-SUGAR, METHODS OF ANALYSIS, AND DETECTION OF ADULTERATION.

BY JULIUS HORTVET.

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BY A rough classification, accountable by the fact that sucrose constitutes their chief ingredient, so-called maple-syrup and maple-sugar have long been classed with products obtained from sugar-cane, sugar-beet and sorghum. The statement that the sugar of the maple sap is identical in composition with that of the sugar-cane has been currently accepted, hence it has been concluded that chemical methods are helpless as a means of distinguishing the syrup or sugar prepared from the sugar-maple from like products prepared from the sugar-cane. Commercial interests have taken advantage of the unsatisfactory state of chemical knowledge regarding maple products, and have been active in

[1] This Journal, **24**, 624 (1902).
[2] *Ber. d. chem. Ges.*, **37**, 1628 (1904).

enforcing upon the popular mind the belief that pure maple-sugar is chemically identical with the well-known refined granulated sugar. Contrary to absurd opinions and interested claims, however, it is obvious that, beyond the point of identity as regards their sucrose content, so-called cane-sugar and maple-sugar are very divergent in composition and properties.

Maple-sap is essentially a dilute solution of sucrose, carrying, also, small amounts of proteids, organic acids (mainly malic), mineral matter (chiefly lime and potash) and traces of reducing sugars.[1] During the boiling-down process some of the proteids are coagulated and rise to the surface, where they are removed by skimming, while a considerable amount of the mineral matter (so-called "nitre" or simple dirt) is deposited at the bottom of the evaporator. The syrup, after being drawn, may be further clarified by filtering hot through felt strainers or by sedimentation. A product intended for use as syrup is commonly boiled down to a density of 11 pounds of syrup per gallon; if it is to be made into sugar, the syrup is boiled to a concentration such that it will harden on cooling. As is well known, the value of maple-sugar is out of proportion to the saccharine matter which it contains, and is due to the peculiar pleasant flavor derived from certain minor ingredients carried in the sap. The nature of these flavoring substances has not been definitely determined, but that they are not wholly volatile is shown by the fact that they remain in the syrup during the process of concentration and may be retained in the sugar for a considerable time. The distinctly agreeable odor that accompanies the evaporation of maple-sap is familiar to any one who has visited an orchard during the sugar season. The wide range in color, from very light to very dark, characteristic of maple-syrups and sugars is attributable to various causes, chief among which are location and character of soil, time of season, and care taken in handling and boiling the sap. The first run of sap produces a much lighter-colored syrup and sugar than the later runs, which not only yield darker products, but impart flavors sometimes unpleasant to the taste. The first run is considered by all producers as by far the best for making a first-class product. Color is, however, not a safe criterion as to quality or purity, and has little influence upon prices commanded in the general market, as it has long been suspected that very little of the pure article eventually reaches the consumer.

[1] Vt. Agr. Exp. Sta., Bull. 103, "The Maple Sap Flow," p. 47.

It has long been a matter of common report that there are sold on the market large quantities of alleged maple-syrups which are fabrications composed only in part of maple-syrup, or, as has often been the case, are entirely free from any maple product whatever. The requisite maple flavor has been imparted to such syrups, it is said, by mixing them with an extract prepared from hickory bark and sold extensively under the name of "mapleine." As claimed by its inventor, "The effect of the extract or decoction is to give to the syrup the flavor of the maple, producing a syrup which cannot be distinguished from genuine maple-syrup."[1] The simple practice of flavoring syrups with corn-cob infusions has, so far as known, probably not extended seriously beyond the bounds of rural communities or the domestic kitchen. There has recently been reported a process of preparing imitation maple-syrup, which consists in distilling maple or hickory chips with steam, adding sugar to the distillate, boiling down to the required density, then adding caramel if necessary. Various other processes, concoctions, flavors and essences have presented themselves from time to time, but these, in most instances, have been of such a character as not to merit serious attention. The use of so-called corn-syrup, or starch glucose, as an adulterant of maple-syrup has been practiced quite extensively for many years, but this form of adulteration, while very profitable to the manufacturer, has yielded an inferior article and one which could easily be detected by the chemist, if not by the consumer.

Within the past fifteen years more or less complete analyses of maple products have been made and reported, notably by analysts of the United States Department of Agriculture,[2] the Canada Inland Revenue Department,[3] the Connecticut Agricultural Experiment Station at New Haven,[4] and the Illinois State Food Commission.[5] These analyses, with the exception of those reported from Canada, show little or no attempt to determine the properties of samples of known purity, and beyond the point of reporting adulteration with starch glucose, all analysts are cautious and seem to be of the opinion that it is impossible to say in regard to

[1] U. S. Dept. Agr., Bull. 13, 710-712, 1892.
[2] U. S. Dept. Agr., Bull. 13, 1892.
[3] Inland Rev. Dept., Can., Bull. 1896, Part III.
[4] Conn. Agr. Expt. Sta., New Haven, 20th Annual Rep., 1896.
[5] Ill. Food Com., 2nd Annual Rep., 1901.

most samples whether they are spurious or genuine. The analysis of commercial maple-syrups has, therefore, in recent years, been confined chiefly to the detection of starch glucose.

Of the small number of syrups examined in the laboratory of the Minnesota Dairy and Food Department during 1902 about 10 per cent. were found to be glucose mixtures, and during the progress of the work in the year following it soon became apparent that a very large number of the alleged maple-syrups, not classed among the glucose mixtures, were, in all probability, maple-syrups more or less diluted with common cane-syrup. A complete chemical analysis of a large number of samples of known purity alongside with the analysis of a corresponding number of commercial products seemed to be the necesssary course in order to differentiate more closely the true from the false. During the seasons of 1903 and 1904 about fifty samples of known purity, fairly representing the principal maple-sugar producing regions of the United States, have been collected. The results of the analysis of these, together with results obtained on syrups and sugars bought in the open market, are shown in the following tables. The known pure syrups and sugars include (1) Minnesota syrups obtained direct from the producers by inspectors of this Department; (2) samples obtained by the chemists of this Department through relatives or friends in Eastern States; (3) samples obtained by other persons through reliable sources. Very nearly all samples have been furnished with the understanding that they were to be used for the purpose of a special investigation, and in many cases a written statement has been given in answer to questions regarding the methods employed in making pure maple-syrup and pure maple-sugar.

The descriptive terms used in the tables are for the present purpose general, no attempt being made to give exact dates of manufacture or to state, in detail, the condition or properties of the samples. It is considered sufficient simply to give year, time of season (early, middle or late), and a word as to the appearance, *i. e.*, whether light, medium or dark. In Table I, syrup No. 4 Penn. was reduced to a small residue, composed largely of sedimentary material, at the time of the protein and malic acid determinations. Samples Nos. 59 Minn., 60 Minn., 61 Minn., and 1 N.Y. were spent before the determinations could be completed. The New York syrups were unusually well clarified and were made

with great care, especially for this investigation. The Minnesota, Pennsylvania and Connecticut samples were of average good quality. In Table IV, sugar No. 1 N. Y. was of uncommonly light shade, and when pulverized might have been mistaken for a fair grade of refined cane-sugar. Samples Nos. A Vt., B Vt. and C Vt. were of somewhat inferior grade and were evidently made with little attempt at clarifying. All other sugars were of good quality, especially 3 N. Y., which came from the same source as the New York syrups above mentioned. Sample No. 3*b* Penn. was too small to permit of a complete analysis.

While undergoing analysis the syrups were kept in cans or bottles in the refrigerator. In a few cases where it seemed necessary, the tendency to fermentation was overcome by the use of antiseptics. Formaldehyde, salicylic acid and benzoic acid were tried, each with fairly good results, though it was recognized that in certain contingencies each might be objectionable, formaldehyde, for example, on account of its reducing action on the Fehling solution, being inadmissible in cases where reducing sugars were yet to be determined. To insure a satisfactory keeping of the sugar samples, it was found advisable to break them up in lumps, then place them in wide-mouthed bottles and keep tightly corked. In sampling the syrups for analysis the clear liquid was taken, avoiding the sedimentary material. When a sample could not be clarified by sedimentation, it was filtered through ordinary filter-paper under pressure. In sampling a sugar, a portion of the mixed shavings, obtained from several pieces, was taken.

METHODS OF ANALYSIS.

Specific Gravity.—The syrup was cooled to 15.5° C. and the determination made with a specific gravity hydrometer graduated from 1,200 to 1,400.

Moisture.—Three grams of the sample were weighed into a flat-bottomed glass dish having a diameter of about 8 cm. and provided with a short glass stirring rod. In the case of a sugar the sample was added in a finely shaven condition, and in every case the sample was so placed as to cover the bottom of the dish evenly in a thin layer. The sample was dried at the temperature of boiling water, stirred at two-hour intervals until brought to a powdered condition, then at the end of eight hours cooled in a desiccator and weighed. The sample was returned to

TABLE I.—PURE MAPLE-SYRUPS.

Sample number.	Description.	Results on original sample.																		Results on dry sample.			
		Specific gravity at 15.5° C.	Moisture. Per cent.	Polarization.		Sucrose. Per cent.	Reducing sugar. Per cent.	Lead subacetate precipitate. cc.	Protein, N × 6.25. Per cent.	Malic acid value. Per cent.	Ash.									Ash.			
				Direct.	Invert.						Total. Per cent.	Water-soluble. Per cent.	Phenolphthalein alkalinity.	Methyl orange alkalinity.	Water-insoluble. Per cent.	Water-insoluble alkalinity.	Total alkalinity.	K_2O. Per cent.	CaO. Per cent.	Lead subacetate precipitate. cc.	Total. Per cent.	Phenolphthalein, alkalinity.	Total alkalinity.
59 Min.	1903, early, light	1.293	36.90	+54 6	—20.0	57.09	3.45	1.10	....	...	0.74	0.40	0.34	0.49	0.34	0.66	1.15	0.32	0.13	1.74	1.17	0.53	1.82
60 Min.	1903, early, light	1.315	31.63	+57.2	—20.6	59 54	4.76	1.24	0.288	...	0.67	0.41	0.30	0.51	0 26	0.59	1.10	0.28	0.14	1.83	0.98	0.43	1.60
61 Min.	1903, late, medium	1.293	35.90	+55.4	—21.1	58.55	2.87	1.12	0.251	...	0.86	0.49	0.31	0.61	0.37	0.79	1.40	0.29	0.22	1.74	1.34	0.48	2.18
71 Min.	1903, late, dark	1.306	35.23	+50.4	—21.5	55.02	7.68	1.23	0.249	1.03	0.73	0.48	0.29	0.57	0.25	0.57	1.14	0.27	0.16	1.84	1.12	0.44	1.76
74 Min.	1903, medium	1.316	33.43	+59.4	—21.5	61.91	2.53	1.09	0.250	...	0.53	0.38	0.20	0.41	0.15	0.32	0.73	0.19	0.10	1.63	0.79	0.30	1.09
5 N. H.	1903, medium	1.314	34.20	+59.0	—21.3	60.53	3.56	1.29	0.334	1.09	0.81	0.48	0.33	0.57	0 33	0.66	1.23	0.31	0.16	1.96	1.23	0.50	1.87
1 Penn.	1903, medium	1.331	30.63	+58.6	—20.9	61.62	4.31	1.23	0.243	1.10	0.53	0.32	0.27	0.48	0.21	0.50	0.98	0.20	0.12	1.77	0.76	0.38	1.41
2 Penn.	1903, medium	1.327	32.43	+60.6	—20.2	62.31	3.62	1.20	0.250	1.28	0.77	0.45	0.38	0.63	0 32	0.70	1.33	0.36	0.16	1.78	1.14	0.56	1.96
3 Penn.	1902, early, light	1.293	35.83	+57.4	—20.3	59.95	1.09	1.46	0.229	1.19	0.52	0.21	0.26	0.38	0.31	0.68	1.06	0.24	0 10	2.27	0.81	0.40	1.65
4 Penn.	1903, late, very dark	1.300	34.23	+51.0	—18.1	53.29	9.17	1.76	0.406	1.76	1.01	0.46	0.41	0.66	0.55	0.85	1.51	0.38	0.19	2.67	1.53	0.62	2.14
1 N. Y.	1903, very light	1.306	34.66	+62.4	—18.4	61.83	0.99	1.65	....	...	0.57	0.34	0.23	0.41	0.23	0.53	0.94	0.22	0.13	2.52	0.87	0.35	1.43
I, Wis.	1903, medium	1.309	34.47	+60.2	—21.1	62.70	0.60	1.35	0.251	0.94	0.56	0.31	0.20	0.51	0.25	0.31	0 82	0.22	0.10	2.06	0.85	0.30	1.25
C Min.	1903, medium	1.301	37.13	+57.0	—20.6	58.49	2.92	1.82	0.259	1.04	0.67	0.36	0.24	0.50	0.41	0.72	1.22	0.22	0.20	2.89	1.06	0.38	1.94
1 Min.	1904, early, light	1.296	37.66	+55.7	—21.5	58.19	1.34	1.11	0.258	0.95	0.58	...	0.23	...	...	...	0.99	0.22	0.15	1.78	0.93	0.36	1.58
2 Min.	1904, late, dark	1.336	31.00	+62.2	—23.9	64.90	2.82	1.01	....	1.06	0.64	...	0.26	...	...	...	1.43	0.24	0.20	1.46	0.90	0.36	2.02
5 Penn.	1904, early, light	1.330	31.26	+60.0	—25.4	65.11	1.36	1.22	0.259	1.28	0.65	...	0.24	...	...	..	1.11	0.23	0.18	1.77	0.94	0.34	1.61
6 Penn.	1904, middle, medium	1.326	31.33	+59.0	—25.6	63.53	1.15	1.17	0.262	1.06	0.66	...	0.23	...	...	..	1.03	0.22	0.16	1.70	0.96	0.34	1.50
7 Penn.	1904, late, medium	1.328	33.95	+58.3	—23.6	61.50	2.57	1.24	0.265	1.05	0.67	...	0.28	...	...	...	1.07	0.26	0.14	1.88	1.01	0.42	1.62
2 N. Y.	1904, early, light	1.335	31.93	+59.1	—25 0	63.15	1.32	0.94	0.269	0.88	0.64	...	0.25	...	...	...	1.00	0.23	0.14	1.38	0.94	0.37	1.47
3 N. Y.	1904, late, medium	1.333	31.93	+60.2	—25.6	64.43	1.72	0.99	0.288	0.84	0.66	...	0.23	...	...	...	1.01	0.22	0.15	1.46	0.97	0.33	1.48
1 Conn.	1904, early, medium	1.337	30.23	+61.2	—23.6	63.92	1.14	0.96	0.223	0.85	0.62	...	0.26	...	...	...	0.94	0.24	0.12	1 38	0.88	0.37	1.34
2 Conn.	1904, late, dark	1.340	33.06	+59.3	—22.4	62.05	1.26	1.47	0.233	1.06	0.90	...	0.31	...	...	...	1.09	0.29	0.13	2.19	1.34	0.46	1.63

TABLE II.—ADULTERATED MAPLE-SYRUPS.

Sample number.	Specific gravity at 15.5° C.	Results on original sample.														Results on dry sample.			
		Polarization.			Reducing sugar.	Lead subacetate precipitate.	Protein, N × 6.25.	Malic acid value	Ash.							Ash.			
		Direct.	Invert.	Sucrose.	Per cent.	cc.	Per cent.	Per cent.	Total. Per cent.	Water-soluble. Per cent.	Phenolphthalein alkalinity.	Methyl orange alkalinity.	Water-insoluble. Per cent.	Water-insoluble alkalinity.	Total alkalinity.	K_2O. Per cent.	CaO. Per cent.	Lead subacetate precipitate. cc.	Total. Per cent.	Phenolphthalein alkalinity.	Total alkalinity.
54	1.313	+62.9	—18.2	62.54	1.49	0.27	0.098	0.40	0.05	0.03	0.00	0.02	0.02	0.07	0.09	0.00	0.02	0.42	0.07	0.00	0.14
66	1.326	35.56	32.90	+63.4	—20.2	63.98	2.52	0.87	0.200	0.43	0.18	0.10	0.01	0.13	0.08	0.02	0.10	0.42	0.07	0.00	0.14
72	1.319	34.10	+58.4	—20.4	60.31	3.99	0.95	0.232	0.36	0.24	0.14	0.05	0.18	0.31	0.19	0.38	0.16	0.29	0.04	0.06	0.05	0.05	0.43
95	1.308	34.03	+58.4	—22.2	61.22	2.46	0.85	0.369	0.82	0.42	0.23	0.15	0.31	0.19	0.38	0.69	0.14	0.32	0.05	0.06	1.44	0.36	0.07	0.48
96	1.323	32.70	+63.6	—21.7	64.79	1.92	0.72	0.159	0.31	0.13	0.09	0.03	0.10	0.04	0.12	0.22	0.03	0.05	0.14	0.11	1.29	0.64	0.23	1.05
104	1.321	33.03	+58.6	—18.7	58.71	7.05	0.84	0.185	...	0.15	0.09	0.04	0.22	0.06	0.16	0.38	0.03	0.09	1.25	0.22	0.06	0.56
112	1.317	33.47	+61.4	—19.6	61.52	3.64	0.72	0.168	0.50	0.12	0.08	0.04	0.13	0.04	0.14	0.27	0.04	0.05	1.08	0.18	0.06	0.40
119	1.309	35.43	+53.2	—18.7	55.03	7.52	0.31	0.106	0.38	0.15	0.08	0.02	0.15	0.07	0.09	0.24	0 02	0.02	0.46	0.23	0.03	0.37
236	1.336	31.83	+55.1	—21.2	57.51	7.62	0.23	0.182	0.35	0.19	0.15	0.04	0.11	0.04	0.15	0.26	0.04	0.05	0.33	0.27	0.06	0.38
282	1.331	32.90	+64.8	—20.3	64.63	1.99	0.37	0.163	0.45	0.12	0.07	0.04	0.10	0.05	0.17	0.27	0.03	0.06	0.55	0.17	0.05	0.40
307	1.328	33.20	+65.0	—20.9	65.24	1.73	0.55	0.157	...	0.14	0.08	0.03	0.08	0.06	0.19	0.27	0.03	0.06	0.82	0.21	0.04	0.40
313	1.326	33.55	+57.0	—19.8	58.33	8.14	0.79	0.125	0.24	0.20	0.15	0.05	0.14	0.05	0.19	0.33	0.05	0.06	1.17	0.29	0.07	0.49
314	1.318	36.17	+59.6	—19.1	59.77	1.59	0.24	0.125	0.46	0.07	0.04	0.02	0.04	0.03	0.12	0.16	0.02	0.04	0.37	0.10	0.03	0.25
316	1.326	33.30	+63.2	—21.4	63.77	1.63	0.38	0.163	0.41	0.08	0.01	0.01	0.03	0.04	0.08	0.11	0.01	0.02	0.57	0.12	0.01	0.16
317	1.328	31.33	+65.2	—22.2	65.88	3.36	0.78	0.158	0.60	0.25	0.10	0.06	0.14	0.15	0.32	0.46	0.06	0.09	1.13	0.36	0.09	0.67
318	1.332	31.50	+66.0	—22.6	66.78	1.45	0.27	0.133	0.45	0.07	0.03	0.01	0.04	0.04	0.10	0.14	0.01	0.03	0.39	0.10	0.01	0.20
321	1.325	33.50	+62.4	—22.0	63.62	2.16	0.95	0.290	0.51	0.34	0.21	0.10	0.25	0.13	0.29	0.54	0.09	0.09	1.42	0.51	0 15	0.81
364	1.343	30.16	+54.0	—20.4	56.08	12.47	0.76	0.193	0.53	0.20	...	0.08	...	...	...	0.35	0.07	0.05	1.08	0.28	0.11	0.50
371	1.328	33.23	+62.9	—22.0	63.99	2.34	0.60	0.196	0.37	0.17	...	0.06	...	...	...	0.31	0.06	0.05	0.90	0.25	0.06	0.47

TABLE III.—PURE MAPLE-SUGARS.

Sample number.	Description.	Results on original sample.																	Results on dry sample.			
			Polarization.							Ash.									Ash.			
		Moisture. Per cent.	Direct.	Invert.	Sucrose. Per cent.	Reducing sugar. Per cent.	Lead subacetate precipitate. cc.	Protein, N × 6.25. Per cent.	Malic acid value. Per cent.	Total. Per cent.	Water-soluble. Per cent.	Phenolphthalein alkalinity.	Methyl orange alkalinity.	Water-insoluble. Per cent.	Water-insoluble alkalinity.	Total alkalinity.	K_2O. Per cent.	CaO. Per cent.	Lead subacetate precipitate. cc.	Total. Per cent.	Phenolphthalein alkalinity.	Total alkalinity.
3*a* Penn.	1903, early	6.07	+87.4	—28.1	89.53	2.22	2.30	0.379	1.32	0.75	0.43	0.44	0.74	0.32	0.66	1.40	0.41	0.15	2.44	0.79	0.46	1.49
3*b* Penn.	1903, early	7.00	+83.2	—27.5	85.81	4.45	...	....	...	0.76	0.44	0.34	0.59	0.32	0.69	1.28	0.32	0.17	...	0.81	0.36	1.37
1 N. Y.	1903, early, very light	12.73	+82.4	—25.9	82.88	1.16	2.01	0.408	1.24	0.77	0.37	0.33	0.56	0.40	0.77	1.33	0.31	0.19	2.30	0.88	0.37	1.52
1 Vt.	1903, early, medium	14.06	+72.6	—25.9	74.25	7.25	2.05	0.641	...	0.81	0.33	0.36	0.59	0.48	1.10	1.69	0.34	0.27	2.38	0.94	0.41	1.96
1 N. H.	1903, light	7.87	+81.8	—28.8	85.73	4.25	2.64	0.525	1.14	1.16	0.67	0.45	0.78	0.49	1.10	1.88	0.42	0.27	2.86	1.25	0.48	2.04
2 N. H.	1903, middle, medium	6.03	+85.0	—29.2	88.52	3.69	3.15	0.466	1.49	1.05	0.50	0.54	0.95	0.55	1.18	2.13	0.51	0.29	3.35	1.11	0.57	2.26
M. Vt.	1903, late, dark	15.67	+78.8	—27.9	80.43	1.92	3.16	0.437	1.43	1.16	0.42	0.40	0.55	0.74	1.28	1.83	0.38	0.29	3.74	1.37	0.47	2.17
O. N. Y.	1904, medium	4.27	+79.8	—28.4	84.85	8.37	2.40	0.641	...	0.83	0.36	0.37	0.55	0.47	0.85	1.40	0.35	0.18	2.50	0.86	0.38	1.46
A. Vt.	1903, early, light	7.97	+85.6	—29.7	86.26	1.23	2.86	0.700	1.67	1.03	0.45	0.41	0.63	0.58	1.14	1.77	0.38	0.18	3.10	1.11	0.44	1.92
B. Vt.	1903, middle, medium	6.97	+83.8	—30.5	85.51	2.96	4.41	0.700	1.60	1.20	0.47	0.47	0.60	0.73	1.45	2.05	0.44	0.31	4.74	1.29	0.50	2.20
C. Vt.	1903, late, very dark	10.50	+80.2	—28.6	81.40	3 35	3.66	0.816	1.64	1.30	0.52	0.46	0.68	0.78	1.46	2.14	0.43	0.34	4.09	1.45	0.51	2.39
F. N. H.	1904, early, very light	8.90	+84.7	—31.0	87.21	1.69	1.94	0.437	1.45	0.83	...	0.34	...	...	...	1.50	0.32	0.23	2.13	0.91	0.37	1.64
2 Vt.	1904, early, medium	14.73	+79.3	—30.0	82.39	1.78	1.25	0.350	0.98	0.71	...	0.31	...	...	...	1.31	0.29	0.28	1.46	0.83	0.36	1.53
1 Penn.	1904, early, light	6.33	+86.0	—27.2	88 84	1.90	1.40	0.408	1.13	0.76	...	0.36	...	...	...	1.36	0.44	0.28	1.49	0.81	0.38	1.45
2 Penn.	1904, middle, medium	7.40	+83.9	—29.0	88.60	1.86	1.50	0.437	1.04	0.81	...	0.41	...	...	...	1.45	0.38	0.29	1.62	0.87	0.44	1.56
3 Penn.	1904, late, medium	7.06	+82.3	—29.4	87.53	3.23	1.60	0.408	1.18	0.88	...	0.43	...	...	...	1.56	0.45	0.32	1.72	0.94	0.46	1.67
3 N. Y.	1904, late, medium	9.83	+80.2	—30.4	84.32	1.40	1.18	0.437	1.08	0.65	...	0.31	...	...	...	1.18	0.29	0.15	1.31	0.72	0.34	1.30
1 Conn.	1904, early, medium	7.96	+85.7	—29.0	86.46	2.18	1.39	0.320	1.06	0.78	...	0.23	...	...	...	1.03	0.21	0.16	1.51	0.84	0.25	1.12
2 Conn.	1904, late, very dark	6.80	+78.4	—28.0	80.20	6.39	1.53	0.408	1.14	0.99	...	0.29	...	...	...	1.09	0.2;	0.14	1.64	1.06	0.31	1.17

TABLE IV.—ADULTERATED MAPLE SUGARS.

Sample number.	Results on original sample.																		Results on dry sample.			
		Polarization.						Ash.											Ash.			
	Moisture. Per cent.	Direct.	Invert.	Sucrose. Per cent.	Reducing sugar. Per cent.	Lead subacetate precipitate. cc.	Protein, N × 6.25. Per cent.	Malic acid value. Per cent.	Total. Per cent.	Water-soluble. Per cent.	Phenolphthalein alkalinity.	Methyl orange alkalinity.	Water-insoluble. Per cent.	Water-insoluble alkalinity.	Total alkalinity.	K_2O. Per cent.	CaO. Per cent.	Lead subacetate precipitate. cc.	Total. Per cent.	Phenolphthalein alkalinity.	Total alkalinity.
216	7.66	+87.6	—27.9	88.39	2.68	1.40	0.233	...	0.37	0.17	0.12	0.23	0.20	0.28	0.51	0.19	0.08	1.51	0.40	0.13	0.55
M. 11	5.70	+91.6	—29.7	91.43	2.63	0.10	0.320	0.25	0.10	0.06	0.02	0.06	0.04	0.11	0.34	0.02	0.04	0.10	0.10	0.02	0.36
344	5.73	+88.6	—30.8	90.00	3.28	1.29	0.349	0.80	0.36	0.17	0.11	0.22	0.19	0.46	0.68	0.10	0.13	1.36	0.38	0.11	0.72
303	6.40	+85.2	—29.2	86.28	4.74	1.05	0.262	0.17	0.26	...	0.08	...	...	...	0.37	0.07	0.06	1.12	0.27	0.08	0.39
365	2.43	+91.5	—30.8	92.19	4.39	0.87	0.175	0.55	0.20	...	0.08	...	...	...	0.39	0.08	0.06	0.89	0.20	0.08	0.40
480	...	.....	.....	....	...	1.03	....	0.31	1.76	...	0.42	...	...	...	1.22	0.39	0.11	...	...	...	...

the oven and dried for another two hours. If, on again weighing, there was noted only a slight change in weight, the drying was considered finished; otherwise the drying was continued until the weight was practically constant.

Polarization (Sucrose).—The German official method[1] was used, as recommended on page 57 of the Proceedings of the Association of Official Agricultural Chemists for 1902, and with the modification given on page 230 of the Proceedings for 1903. The alternate official method of inversion without the application of heat is commended. The absence of raffinose may be assumed, and the polarizations should be made in a tube provided with a water jacket, as devised by Landolt, passing a current of water through to maintain a temperature of 20° C.

Reducing Sugars (Estimated as Dextrose).—The determination was made by the method of Allihn,[2] or, in other words, by the official method of 1901,[3] omitting the clarification with lead subacetate. The solution of the sample was filtered, when necessary, through a dry filter and made up so as to contain approximately 1 per cent. of reducing sugar. The precipitated copper oxide was washed with alcohol and ether, dried at 100° C. for one hour, allowed to cool one-half hour, then weighed as Cu_2O. The clarification with subacetate of lead has been omitted, as it has been found that results on clarified and on unclarified solutions, prepared from the same sample, agree closely.

Lead Subacetate Precipitate.—The wide variation in the volumes of the precipitates formed when clarifying maple-sugar and syrup solutions with subacetate of lead has often been noted. It has been observed that more or less copious precipitates were associated with samples of known purity, while in very many cases of known or suspected adulteration with cane-sugar the precipitates were slight or only equivalent to a mere cloudiness. A year ago a method was devised by which these precipitates could be made to occupy definite volumes under fixed conditions. The method, in brief, consists in reducing the precipitate to a compact mass at the bottom of a graduated tube by

[1] Wiechmann's "Sugar Analysis," p. 45.
[2] Bull. 46, U. S. Dept. Agr., Bureau of Chemistry, p. 35.
[3] Bull. 65, U. S. Dept. Agr., Bureau of Chemistry, p. 49.

the use of a centrifugal machine, noting the reading on the tube, applying necessary corrections, and expressing the volume of the precipitate in cubic centimeters and tenths. By means of this method it has been shown that valuable data are readily obtainable regarding the character of suspected samples.

The apparatus consists of a glass tube somewhat suggestive of an inverted Babcock cream test bottle (see cut), and is described as follows:

Total length	15.2 cm.
Diameter (wide part)	3.0 "
Diameter (neck)	2.0 "
Stem graduated to 5 cc. and tenths; 5 cc. division line 5 mm. below beginning of wide part.	
Ground area on wide part for use in numbering.	

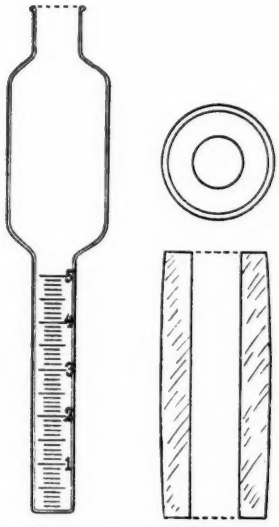
The tube is provided with a holder, which is described as follows:

Length	7.7 cm.
Diameter	3.2 to 3.5 cm.
Center hole, to fit stem	1.3 cm. diameter.
Made of pine or white wood.	

The tube and holder constitute a couple and weigh together about 50 grams. They should be so constructed that when fitted together the bottom end of the tube will be exactly even with the lower surface of the holder. In order to prevent mixing the pieces belonging to a set, each tube should bear a number corresponding with the number of its holder. Also, in a set, each couple, *i. e.*, tube and holder, should be made to balance every other. There should be, as nearly as possible, a balanced load carried at the circumference of the wheel of the centrifuge.

The determination was conducted as follows: Five cc. of syrup or 5 grams of sugar were introduced into the tube, 10 cc. of water added, and the contents thoroughly mixed. Time was given in the case of sugar for complete solution.

One-half cc. (10 drops) of alumina cream (prepared as given in Bulletin No. 46, page 39) and 1.5 cc. of lead subacetate were



Tube. Holder.

Apparatus.[1]

then added and the contents well shaken. The mixture was allowed to stand from forty-five to sixty minutes, occasionally giving the tube a twisting motion to facilitate the settling of the precipitate.

The tube with its holder was then placed in the centrifugal machine and run six minutes (see conditions given below). At the end of six minutes the contents of the tube were examined, and if any material adhered to the side of the wider portion, it was loosened by means of a small wire provided with a loop at the end. The tube was returned to the centrifuge and run six minutes longer at the same rate. The volume of the precipitate was noted, estimating 0.01 cc. as closely as possible. A blank, using water[2] and the reagents named above, was run as often as seemed necessary in order to be certain as to its value. The blank reading was subtracted from the reading given by the precipitate in each case. In the case of a syrup the result was reduced to the 5-gram basis by dividing by the specific gravity of the sample. If the sugar content of the sample was known, the specific gravity

[1] Circular U. S. Dept. Agr., Bureau of Chemistry, giving Hortvet method for examination of maple-syrup and sugar.

[2] Cane-sugar solution of sp. gr. 1.330 is suggested; the blank would be a trifle higher.

was found from tables.[1] Usually 1.330 has been found very nearly correct for maple syrup.

The centrifugal machine used in this laboratory has a radius of 18.5 cm., and a speed of 1600 revolutions per minute has been adopted. Calling M unity in the formula

$$F = \frac{Mv^2}{r}, \text{ then } F = \frac{v^2}{r}, \text{ and } v = \sqrt{Fr}.$$

From the above a numerical expression for F can be computed, then having measured r for a given machine, the value of v and the required number of revolutions per minute can be found.

The results given in Table V show why a total run of twelve minutes was adopted. Such results can possibly be made to agree more closely under more perfect conditions. The results were obtained on 5 cc. samples and have not been reduced to results on the 5-gram basis. The mean blank at the end of twelve minutes was 0.44 cc. Samples designated 100 per cent. pure are from syrups of known purity. Cane-sugar syrup of the same density was added to the other samples in the proportions indicated.

TABLE V.—PRECIPITATES OBTAINED BY VARYING TIME OF RUNNING.

Purity. Per cent.	Reading six minutes.	Computed reading.	Difference.	Reading eight minutes.	Computed reading.	Difference.	Reading ten minutes.	Computed reading.	Difference.	Reading twelve minutes.	Computed reading.	Difference.
100	2.85	...	...	1.74	...	...	1.45	...	...	1.31	...	...
75	1.35	2.14	0.79	1.21	1.30	0.09	1.09	1.08	0.01	1.01	0.98	0.03
50	1.05	1.42	0.37	0.94	0.87	0.07	0.88	0.72	0.16	0.81	0.65	0.16
25	0.70	0.71	0.01	0.65	0.43	0.22	0.59	0.36	0.23	0.53	0.32	0.21
Blank	0.60	...	...	0.51	...	...	0.50	...	...	0.49	...	...
100	2.50	...	...	1.51	...	...	1.22	...	...	1.17	...	...
60	1.65	1.50	0.15	1.21	0.90	0.31	1.02	0.73	0.29	1.00	0.70	0.30
40	0.89	1.00	0.11	0.74	0.60	0.14	0.67	0.49	0.18	0.63	0.47	0.16
20	0.30	0.50	0.20	0.30	0.30	0.00	0.27	0.24	0.03	0.27	0.23	0.04
Blank	0.40	...	...	0.39	...	...	0.38	...	...	0.38	...	...

Protein.—Nitrogen was determined by the Gunning method, and the protein was computed as N × 6.25. Three grams of sugar, or in case of syrup, about four grams, were weighed into a 500 cc.

[1] Bull. 65, U. S. Dept. Agr., Bureau of Chemistry, Table VI, p. 139.

digestion flask, the sample treated with 10 grams of potassium sulphate and 20 cc. of concentrated sulphuric acid, and the material digested until colorless. After cooling and adding 100 cc. of water the digestion flask was connected with an apparatus for distilling in a current of steam.[1] Seventy cc. of a saturated solution of sodium hydroxide were then run into the flask, steam turned on, and the ammonia distilled into 100 cc. of water containing 5 cc. of tenth-normal sulphuric acid. When about 150 cc. of distillate had been collected, the solution was titrated with tenth-normal sodium hydroxide, using cochineal as an indicator. A blank determination was made and the result applied as a correction factor in making the calculations.

Malic Acid Value.—This determination was made by a modification of the calcium chloride method of Leach and Lythgoe.[2] Six and seven-tenths grams of the sample were weighed into a 200 cc. beaker, and water added to make a volume of 20 cc. The solution was made slightly alkaline with ammonia, 1 cc. of a 10 per cent. solution of calcium chloride added, then 60 cc. of 95 per cent. alcohol. The beaker was covered with a watch-glass and heated for one-half hour on a water-bath, the flame then turned off and the beaker allowed to stand over night. The material in the beaker was then filtered through good quality filter-paper, the precipitate washed with hot 75 per cent. alcohol to freedom from soluble calcium salt, dried and ignited. From 15 to 20 cc. of tenth-normal hydrochloric acid was added to the ignited residue, the lime thoroughly dissolved by careful boiling, and the excess of acid titrated with tenth-normal sodium hydroxide, using methyl orange as an indicator. One-tenth of the number of cubic centimeters of acid neutralized expresses the result, which, for the present, will be called the "malic acid value."

It is not advisable to filter before adding the alcohol, nor has it been found necessary, as no precipitate appears at that point. Repeated trials have also shown that heating to boiling and filtering immediately after adding calcium chloride and alcohol not only incurs a possible loss of material due to bumping, but gives results which are always lower and are seldom concordant. The method has given satisfactory results on a wide range of samples, yet it is not claimed at the present stage of the investiga-

[1] This Journal, **24**, 388 (1902).
[2] *Ibid.*, **26**, 380 (1904).

tion that the results express absolutely the malic acid present; they are given only as "values" which are shown to be significant.

Ash.—Ten grams of the sample were weighed in a tared flat-bottomed platinum dish of about 7 cm. diameter, heated carefully over an asbestos plate until near the point of charring, then ashed until nearly decarbonized at faint redness over a Chaddock burner, being careful not to heat to fusing. Remaining particles of carbon were removed by cooling, adding a few drops of water, drying over the asbestos plate, then heating over the open flame at dull redness. The operation was repeated, if necessary, the dish then cooled in a desiccator and weighed. The weighings were made as quickly as possible, as the ash absorbs moisture very rapidly.

Alkalinity of Ash; Method (a).—Water was added to the ash in the platinum dish, the contents heated nearly to boiling, filtered, and the residue washed until the filtrate and washings amounted to 60 cc. The solution was titrated with tenth-normal hydrochloric acid at ordinary temperature, first with phenolphthaleïn as an indicator, then to the point of complete neutralization with methyl orange as an indicator. The filter-paper and contents were placed in the platinum dish, gently ignited and weighed. After correcting for the weight of the ash of the filter-paper, the percentages of water-insoluble ash and water-soluble ash were calculated. Excess of tenth-normal hydrochloric acid was added to the residue in the dish, the solution heated gently, cooled and titrated with tenth-normal sodium hydroxide, using methyl orange as an indicator. The three alkalinities thus obtained are known respectively as the phenolphthaleïn alkalinity of the water-soluble ash, the methyl orange alkalinity of the water-soluble ash and the alkalinity of the water-insoluble ash, and each is expressed as the number of cubic centimeters of tenth-normal acid used for the ash of 1 gram of the sample.

Method (b).—The platinum dish containing the weighed total ash was nearly filled with water, then warmed gently and well rubbed with a rubber-tipped rod. The solution was titrated in the dish with tenth-normal hydrochloric acid, using phenolphthaleïn as an indicator. It was found that concordant results can be obtained by titrating immediately, allowing the acid to drop into the solution at a uniform rate, stirring continually, and noting the volume run in when the solution first becomes colorless. The

red color soon returns, but the first reading should be the one used. An excess of acid was then added, using at least 2 cc. for each milligram of ash, the solution transferred to a small beaker, care being taken to dissolve out all the ash, and titrated with tenth-normal sodium hydroxide. The two alkalinities thus obtained are known respectively as the phenolphthaleïn alkalinity of the water-soluble ash and the total alkalinity of the ash, and each is expressed as the number of cubic centimeters of tenth-normal acid required for the ash of 1 gram of the sample. The phenolphthaleïn alkalinity values obtained by methods (*a*) and (*b*) agree very closely, and the sum of the two methyl orange alkalinities obtained by method (*a*) obviously equals the total alkalinity obtained by method (*b*).

DISCUSSION AND FURTHER ANALYSES.

Polarization.—As a rule, the pure maple-syrups and sugars show less dextro-polarizations and greater laevo-polarizations than are shown in the adulterated samples, and a common characteristic noted in samples to which cane-sugar has been added is the closer agreement between the sucrose values and the direct polarization readings. In twenty-one samples among the pure maple-syrups and in seventeen samples among the adulterated syrups the sucrose values exceed the direct polarizations, but in the former class the differences range from 1.49 to 5.11, while in the latter class the range is from 0.11 to 2.82. A similar comparison can be made among the results obtaned on the sugars. A close concordance is not shown between the polarization peculiarities and the percentages of reducing sugars.

Reducing Sugars.—The reducing sugars in the pure syrups range from 0.60 to 9.17 per cent., and in the pure sugars from 1.16 to 8.37 per cent. The highest reducing sugar found was in an adulterated syrup, which showed 12.47 per cent. The percentage of reducing sugar is, when taken alone, not a criterion as to purity, and may be related to other causes than adulteration with glucose. In Table VI are given the results obtained in an experiment in which a sample of pure maple-syrup was subjected to a series of boilings covering a total time of forty-five hours. The analyses were made at five-hour intervals. Three months elapsed between the thirty-hour and thirty-five-hour periods, and in the meantime the sample fermented. The sample was boiled in a flask connected with a reflux condenser.

TABLE VI.—RESULTS OF BOILING EXPERIMENT.

Time. Hours.	Polarization. Direct.	Polarization. Invert.	Sucrose. Per cent.	Reducing sugar. Per cent.	Total sugar. Per cent.	Sucrose in total sugar. Per cent.	Reducing sugar in total sugar. Per cent.
.	Original	sample	40.35	1.67	42.02	96.01	3.99
5	+38.0	—14.5	39.47	2.35	41.82	94.31	5.69
10	+36.0	—13.6	37.15	3.60	40.75	91.16	8.84
15	+34.0	—12.2	34.73	6.04	40.77	85.18	14.82
20	+26.9	—11.8	29.10	11.12	40.32	74.07	25.93
25	+20.2	—11.2	23.43	17.09	40.52	57.82	42.18
30	+14.0	—11.2	18.82	21.44	40.26	46.77	53.23
35	+ 2.5	—11.2	10.76	26.75	37.51	28.69	71.31
40	— 4.5	—13.1	6.57	30.89	37.46	17.54	82.46
45	— 9.0	—10.2	0.28	37.25	37.53	0.78	99.22

Lead Subacetate Precipitate.—The precipitates vary in the pure syrups from 0.94 to 1.82 cc., and in the pure sugars from 1.18 to 4.41 cc. The highest results, especially among the sugars, are apt to occur in samples which have not been properly clarified. In well clarified samples the precipitates will be found, as a rule, between 1.00 and 1.20 cc. for syrups, and between 1.20 and 2.00 cc. for sugars. Dilution by adding cane-sugar brings the precipitate values down, a point well illustrated by the results shown in Tables II and IV. The precipitates given by the pure samples were commonly white or very light gray in color, while the supernatant liquid, in practically every case, was clear and colorless. Distinct dark colors have often been observed when making tests on adulterated samples, and these colors have been shown to be due to the presence of caramel.

Protein.—These results are of interest, although they are obtained by a more complete analysis than is usually called for in practical work. The percentages in the pure syrups range from 0.223 to 0.334 (excluding 0.408 obtained on 4 Penn.), and in the pure sugars from 0.320 to 0.816. The results on the adulterated samples are not as low as would be expected in some cases, yet they are, in the main, concordant with the results obtained by the other determinations. The protein content may be lowered by two operations, first by clarification, second by dilution with cane-sugar. It may, therefore, be seen that the protein percentage alone furnishes a clue as to the character of a given sample.

Malic Acid Value.—This determination affords interesting data, and is of great value in doubtful cases. The results on the pure syrups range from 0.84 to 1.28 (excluding 1.76 obtained on

4 Penn.), and on the pure sugars from 0.98 to 1.67. When the results fall below these minimum values there is evidence of adulteration with cane or so-called brown sugar. A good case in point is sample No. 480 in Table IV, in which the malic acid value is 0.31, while the percentage of ash is 1.76. The presence of brown sugar is further indicated in this sample by the relatively low lead subacetate precipitate, also by the high K_2O in comparison with the low CaO. It is safe to say that in the majority of cases the malic acid value furnishes absolute evidence as to whether a sample contains brown sugar. The malic acid values for the brown sugars, tabulated in Table IX, vary from 0.08 to 0.18.

Ash.—The determination of ash is of especial value both as a means of deciding upon the general character of a sample and in detecting adulteration. Unclarified samples are much less uniform in composition than clarified samples, hence the percentages of ash among the former will show wider variations than among the latter. The ash results obtained on pure clarified maple-syrups and sugars should vary within narrow limits. The tabulated results show a variation among the pure syrups from 0.52 to 1.01 per cent., and among the pure sugars from 0.65 to 1.30 per cent. An inspection of the tables, however, shows that the variation among pure clarified samples is not so great, that the proper range for syrups is from 0.52 to about 0.75 per cent., and for sugars from 0.65 to about 1.00 per cent. Percentages of ash furnish, also, fairly definite values upon which to base estimates of the extent of adulteration with cane-sugar, and in making such estimates, say in the case of syrups, it is very fair to assume 0.50 per cent. as the minimum for ash. A safe estimate could be made in the majority of cases, using 0.60 per cent. as representing the ash of an average pure maple-syrup.

Table VII shows results obtained by a quantitative analysis of samples of ash prepared from syrups and sugars of known purity. The results obtained on a sample of brown sugar are also given for comparison. In preparing the ash about 200 grams of syrup or sugar were taken, and the operation carried out by ashing portions of the sample separately. The material was heated in a large platinum dish over an asbestos plate to the point of carbonization, the mass carbonized at low heat, the soluble salts then dissolved in

hot water, filtered and washed out. The residual mass was burned until free from carbon, the solution of the soluble salts added, the whole evaporated to dryness on a water-bath, then, after being gently ignited, placed in a glass-stoppered weighing bottle for future use. The determinations were made by the usual approved methods employed in quantitative analysis.

TABLE VII.—COMPOSITION OF ASH OF MAPLE-SYRUP AND SUGAR.

Samples.	Silica and sand.	CO_2.	CaO.	MgO.	Mn_3O_4.	K_2O.	Na_2O.	SO_3.	P_2O_5.	Cl.
Minnesota syrup	2.25	30.86	18.60	4.65	0.75	31.58	6.86	2.31	1.64	0.09
Penna. syrup...	2.17	28.70	20.35	4.16	2.22	30.87	4.01	2.42	4.67	...
Vermont sugar .	9.77	30.22	23.05	2.54	0.45	28.37	2.84	1.15	1.18	trace
Vermont sugar .	4.48	30.79	20.62	3.75	0.50	33.06	3.56	1.77	1.24	trace
Brown sugar....	2.30	....	15.63	4.72	none	40.62	2.36	4.58	0.32	0.30

The high P_2O_5 result obtained on the Pennsylvania syrup ash is unexpected, yet the result is apparently correct. The result for CO_2 on the brown sugar ash was unsatisfactory, hence is omitted.

The color of the ash of a maple-syrup or sugar is an interesting property. An almost constant indication is a more or less distinct green color, the intensity of which varies partly with the degree of purity of the sample. The ash obtained from the Minnesota syrup of Table VII was especially noticeable, the completely ignited sample presenting a distinct purple hue and imparting a decided color to the water solution. The results given in the above table show the presence of manganese in all samples with the exception of the ash of the brown sugar. The characteristic green color is doubtless due to the presence of manganates formed by the fusion of manganese with the potash. The green mass dissolves in a small quantity of cold water to a green solution. When this solution is either acidified, or warmed, or even highly diluted with water, its color changes from green to pink, owing to the conversion of manganate to permanganate.

The high SO_3 result obtained on the brown sugar ash, shown in Table VII, raised the question as to another possible distinction between maple-sugar and brown cane-sugar. The results in Table VIII have been obtained by repeated trials, and show the extent to which this point has been investigated in this laboratory to date. Results are expressed as per cent. on the whole sample.

TABLE VIII.—SO_3 IN BROWN SUGAR, MAPLE-SUGAR, AND MAPLE-SYRUP.

Brown sugars.		Maple-sugars.		Maple-syrups.	
(1) Very light	0.026	2 Penn., 1903	0.019	2 N. Y., 1904	0.033
(2) Medium	0.064	2 Vt., 1904	0.025	6 Penn., 1904	0.036
(3) Medium	0.058	2 N. H., 1904	0.018	1 Minn., 1904	0.023
(4) Dark	0.059	O, N. Y., 1903	0.014	2 Conn., 1904	0.026
		2 Conn., 1904	0.022		
Mean,	0.052		0.019		0.029

No explanation can be given for the fact that the results obtained on the syrups exceed those obtained on the maple-sugars.

In Table IX are shown results of a partial analysis of the four samples of brown sugar included in the preceding table. The chief characteristics shown are, first, very low malic acid values, second, low precipitates in relation to high percentages of ash. It has also been noted that the ash of brown sugar is sometimes difficult to decarbonize, owing to the large amount of fused potash present, and is finally decidedly white.

TABLE IX.—RESULTS OBTAINED ON BROWN SUGARS.

Sample.	Ash. Per cent.	Water-soluble ash. Per cent.	Water-insoluble ash. Per cent.	Phenolphthalein alkalinity.	Methyl orange alkalinity.	Lead subacetate precipitate. cc.	Protein, N × 6.25. Per cent.	Malic acid value.
(1) Very light	0.59	0.46	0.13	0.15	0.32	1.03	0.321	0.08
(2) Medium..	1.65	1.23	0.42	0.29	0.43	1.20	0.340	0.10
(3) Medium..	1.81	1.42	0.39	0.36	0.44	1.45	0.422	0.18
(4) Dark.....	0.85	0.64	0.21	0.23	0.39	1.25	0.393	0.18

Alkalinity of Ash.—As will be seen from Table VII, the composition of the ash of maple-syrups and sugars is characteristic. The ash consists chiefly of the carbonates of potassium and calcium, hence, as might be expected, the alkalinity, whether with phenolphthaleïn or with methyl orange, is characteristic and may be treated as an indication of the purity of a sample. The phenolphthaleïn alkalinities among the pure maple-syrups range from 0.20 to 0.41, and among the pure sugars from 0.23 to 0.54; with the total alkalinities the range is respectively from 0.73 to 1.51, and from 1.03 to 2.14. The K_2O and CaO results shown in Tables I to IV are estimates based on the titrations, and, while close accuracy is not claimed for them, they are given as a matter of general interest.

Effect of Clarification.—In the manufacture of maple-syrup and sugar the mineral and organic substances contained in solution in the sap are only partly separated from the finished product. Interesting results have been obtained by a series of filtering and boiling experiments, the purpose of which was to obtain data showing the changes in general composition occurring in a syrup during the process of clarification. The results are shown in Table X, and need no explanation further than that the syrups were made in the laboratory from known-pure maple-sugar stock.

TABLE X.—RESULTS OBTAINED ON FILTERED AND BOILED SYRUPS.

Description.	Ash. Per cent.	Phenolphthalein alkalinity.	Total alkalinity.	Lead subacetate precipitate. cc.	Malic acid value.
Syrup made from early sugar (sp. gr. 1.300)	0.80	0.29	1.37	1.53	1.10
Filtered through linen cloth	0.72	0.28	1.15	1.28	1.02
Filtered through S. & S. 575 hardened paper	0.62	0.22	0.95	0.96	0.86
Boiled 7 hrs. and filtered through S. & S. 575	0.58	0.20	0.77	0.93	0.67
Syrup made from late sugar (sp. gr. 1.312)	1.02	0.27	1.36	1.66	1.10
Filtered through felt only	0.79	0.26	1.12	1.57	0.95
Filtered through S. & S. 575 only	0.84	0.22	1.10	1.60	0.91
Same boiled and filtered through S. & S. 575	0.76	0.23	1.26	1.23	0.79
Syrup made from late sugar (sp. gr. 1.253)	0.66	0.20	1.00	1.14	1.19
Filtered through felt only	0.53	0.18	0.98	1.10	1.08
Filtered twice through S. & S. 575 only	0.57	0.16	0.95	1.14	0.92
Same boiled and filtered through S. & S. 575	0.56	0.15	0.96	1.14	0.82

The filtering through hardened filter-paper was accomplished by the aid of a vacuum pump.

Standards of Purity.—On account of its rapidity of execution, the first determination to make in the routine examination of maple products for adulteration is the precipitate with lead subacetate. In doubtful cases this result may be confirmed either by the determination and examination of the ash or by the determination of the malic acid value. In still more doubtful cases and in cases where litigation is involved a full analysis may be required. An inspection of the tabulated results will reveal the extent to which the moisture content of the samples is a factor affecting the magnitude of the results, and will show that standards of purity can best be found among results expressed on the

moisture-free basis. The values tabulated in the last four columns of Tables I to IV will illustrate, and for the purpose of suggesting standards, are briefly summarized as follows:

TABLE XI.—SUMMARY OF RESULTS ON DRY BASIS.

	Syrups.				Sugars.			
	Lead subacetate precipitate. cc.	Ash. Per cent.	Phenolphthalein alkalinity.	Total alkalinity.	Lead subacetate precipitate. cc.	Ash. Per cent.	Phenolphthalein alkalinity.	Total alkalinity.
Maximum .	2.89	1.53	0.62	2.18	3.35[1]	1.45	0.57	2.39
Minimum..	1.38	0.76	0.30	1.09	1.31	0.72	0.25	1.12
Mean.....	1.87	1.02	0.40	1.69	1.99	0.99	0.41	1.69

Color.—The more or less marked reaction with ferric salts shown by maple-syrups and maple-sugar solutions is indicative of the presence of tannin. In a few instances the reactions have been noted as slight, but in the majority of samples they have been described as distinct, normal, strong or very strong. In adulterated samples the reactions have been similar, although in a few cases they were so indistinct as to be classed doubtful. Numerous qualitative tests have failed to give results sufficiently definite to aid one in forming an opinion as to the character of a given sample. Pure syrups, as a rule, show little loss of color on filtering through fuller's earth, while among syrups known to be adulterated the loss has often been considerable and in a few cases has amounted practically to a complete removal of the color. Taken in comparison with analytical data, the test with fuller's earth may sometimes give significant results. When the amount of coloring-matter in a sample appears to be high in relation to values which are shown to be low, the fact may be taken as a further proof of sophistication. Qualitative methods here, as elsewhere, are not wholly satisfactory, hence it is hoped in the near future to be able to devise a method by which the examination as to color can be made to furnish definite results.

In conclusion, the writer wishes to acknowledge the assistance received from Mr. F. W. Bedford, of this laboratory, who, in addition to his active interest shown in this investigation, has performed much of the analytical work. He is specially credited

[1] Three unclarified samples omitted.

with the work on the ash alkalinities and on the malic acid values. The results on malic acid are all his. Acknowledgment is also due to Miss Clara Hillesheim for her faithful and efficient assistance in making a large number of the analyses.

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NOTES.

An Experiment Illustrating Osmosis.—If one places an ordinary hen's egg in concentrated hydrochloric acid for a few minutes, the shell is removed and the egg is left in its original shape, surrounded by an excellent semi-permeable membrane.

If now the egg is placed in a beaker of pure water, it will swell up very markedly. For example, an egg weighing 57.8 grams, shelled as indicated, increased in weight in twenty-four hours to 79.0 grams, and in larger circumference from 15.5 to 18.5 cm.

If the egg is placed in a saturated solution of calcium chloride, it will diminish in size just as strikingly. For example, an egg weighing 50 grams decreased in weight in twenty-four hours to 38.8 grams, and in larger circumference from 15.5 to 13.5 cm.

For lecture purposes a very effective arrangement is to get three eggs as nearly the same size as possible, shell them as indicated and place one of them in a calcium chloride solution and the other in water, reserving the third for comparison. At the next lecture attention is called to the change in appearance. The calcium chloride egg will look as if it were cooked.

A still more striking method is to place an egg in a small beaker so that only half of it is immersed in acid. When the half shell is removed the egg is placed in water and in twenty-four hours the unshelled portion will be expanded amazingly and the portion retaining the shell will serve for comparison.

An interesting fact in this connection is that an egg from which the shell has not been removed will increase in weight very materially if placed in pure water for a few hours, but will remain otherwise unchanged. HORACE G. BYERS.

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Preparation of Cyanacetic Ester.—Although cyanacetic ester is a substance of very considerable importance for synthetical work

in organic chemistry, I have been unable to find any satisfactory directions for its preparation. After considerable experience with different mixtures, the following method has been found most satisfactory.

One hundred grams of chloracetic ester (which has been shaken with a solution of sodium carbonate to remove any free chloracetic acid), 54 grams of pure potassium cyanide and 70 cc. of methyl alcohol are put in a flask and boiled with an upright condenser for four hours. The solution is then cooled and sucked off from the potassium cyanide as far as possible, the methyl alcohol distilled away and used for rinsing the potassium cyanide. After distilling the methyl alcohol again from the washings and adding the residue to the main portion, some ether is added to the latter, causing the precipitation of some insoluble matters. The solution is then poured off and fractioned two or three times under diminished pressure. The yield of cyanacetic ester boiling within an interval of about 10° and sufficiently pure for most synthetical purposes is 45 to 55 grams. This is little more than 50 per cent. of the theory, but many other methods which have been tried give lower yields, and, in some cases, only about half as much.

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NEW BOOKS.

RUBBER, GUTTA-PERCHA, AND BALATA. By FRANZ CLOUTH. First English translation, with additions and emendations, by the author. London: Maclaren and Sons; New York: D. Van Nostrand Company. 1903. Price, $5.00 net.

This work is a somewhat enlarged translation of the German edition, and is, in some ways, a disappointing production. It is written by the head of one of the largest of German rubber factories. One would, therefore, naturally expect that, though the book might show deficiencies in its botanical, physical, or chemical sections, in which the author simply shows himself as compiler the technical part of the work would be distinguished from earlier books on the same subject by comprehensive treatment of the ways and means employed in the manufacture of rubber goods. Such a book would be a very acceptable addition to our technical

literature. But just in this respect the book fails entirely. To all those acquainted with the manufacture of rubber goods this will at once be evident from the fact that the manufacture of that enormous variety of articles, classified under the head of soft rubber goods, is disposed of on four pages; the vast amount of technical detail involved in the manufacture of rubber foot-wear is dismissed on one page, and the manufacture of electric cables in even less space. To the student of technology the book is, therefore, of very little use, while to the manufacturer and scientific worker it offers nothing which could not as well, and sometimes better, be found elsewhere. In its general sections Clouth's work follows closely the lines of Seeligmann's earlier work, and it also shows, therefore, some of the latter's shortcomings on the more scientific side of the subject. Thus there is no reason whatever to confine the chapter on the "Coagulation of the Rubber Latex" to the mere statement of the methods employed by the natives, and it can only be described as mischievous to designate the process of coagulation as "decomposition." Again do we find here asserted the solubility of rubber in ether, in which, as a matter of fact, all grades of rubber are entirely insoluble. The statement that "at a higher temperature the dissolving process is perfect, but does not take place without decomposition," is either enigmatical or untrue, possibly both. The way in which the author deals with the question of the nature of vulcanization is, perhaps, heroic, but it is bound to place him in opposition to all those competent to judge this important point.

Seeing that this book is of as little service to the scientific worker as to the student of technology, it might appear surprising that there should have been a demand for an English edition. That there was such a demand, according to the author's own statement in the preface, serves as a striking demonstration of the extraordinary dearth of literature on the subject of rubber and rubber manufacturing.

In defense of the author against part of the above criticism, it may certainly be urged that the writing of an exhaustive work upon India rubber, and the manufacture of rubber goods, would be a gigantic undertaking, if, indeed, it is not beyond the powers of any one man. But this really only goes to show that it is a mistake to write a book of a scope impossible of attainment. As far as the technical side of India rubber is concerned, there ex-

ists, therefore, still a long-felt want of a book dealing, in a comprehensive way, not so much with the manufacture of all imaginable varieties of rubber goods in full detail, but rather confining itself to an exhaustive presentation of the principal general working methods employed in rubber manufacture. Such a book would be of the greatest value to every student of technology, as well as to rubber manufacturers all the world over. C. O. WEBER.

A SYSTEMATIC HANDBOOK OF VOLUMETRIC ANALYSIS. By FRANCIS C. SUTTON. Ninth edition, revised and enlarged. P. Blakiston's Son and Co. 1904. 8vo. xii + 617 pp. Price, $5.00.

It is unnecessary to say anthing of the merits of this new edition of an old and greatly valued book. The eighth edition is dated 1903, which shows that the book is still appreciated. The size of the page has been enlarged in the new edition, which shows signs of careful editing. A new section on the determination of potassium as cobaltrinitrite is given; the section on salt cake has been cut down; five new pages on the compounds in gas liquors have been added; a page is added on the extension of the iodometric system; White's method for determining aluminium sulphate is described; two pages have been added in describing methods for barium; the paragraph on the titration of iron by stannous chloride is replaced by one on the titration of iron by titanous chloride; three pages are added on the azo colors. These and many other deletions and additions make the new edition valuable even to those who have that of 1903. So much has been cut out that the number of pages is a little less than in the eighth edition. A brief bibliography might, with advantage, be added to each chapter. EDWARD HART.